QUANTA CHEMISTRY

An Institute of Chemical Sciences

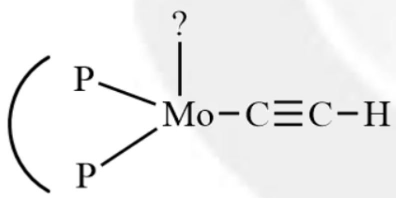
DPP – (1) OMC

1. Formulate neutral 18-electron complexes of chromium which contain only cyclopentadienyl, carbonyl, and nitrosyl ligands.
   (a) $(Cp)_2$ Cr (NO) (CO)   (b) CpCr (NO) $(CO)_2$
   (c) Cp (Cr) $(NO)_2$ CO   (d) Cp Cr (NO) $(CO)_3$

2. Which of the following complex does not follow $18e^{\Theta}$ rule:
   (a) $[Fe(CO)_4]^{2-}$ (b) $[(\eta^5 - C_5H_5)_2 CO]^+$
   (c) $[Ir(pph_3)_2 COCl]$ (d) $[(\eta^3 - C_5H_5)(\eta^5 - C_5H_5) Fe (CO)]$

3. Consider the $18e^{\Theta}$ rule as a guide determine the unknown quantity in the following complex which is 4d series:
   (a) Fe   (b) Ru   (c) Rh   (d) Tc

4. In the following complex what will be the missing ligand which will cyclic, planar conjugated hydrocarbon?



   (a) Cyelopentadiene   (b) tropylium ion   (c) Cyclobutadiene   (d) Cyclohexane.

5. In this complex $[Cp_2W(CO)_2]$ if it follow $18e^{\Theta}$ that what two type of hapticity of Cp is prsent.
   (a) 5, 5   (b) 3, 3   (c) 3, 5   (d) 1, 5

6. Which of the following complex follows $18e^{\Theta}$ rule?
   (a) Cp Fe $(CO)_2$ (b) Cp Mo $(CO)_3$ (c) Cp_2 Co   (c) Cp_2 Ru

7. What will be the oxidation state of W in the given complex of $(Me_3\,CO)_3$ W $(CCMe_3)$.
   (a) + 6   (b) + 5   (c) + 4   (d) + 3

8. Considering $18e^{\Theta}$ rule, the value of Z in this complex $[\eta^5\, Cp\, (CO)_2\, Fe\, (Ph - C \equiv C - H)]^Z$
   (a) + 1   (b) – 1   (c) + 2   (d) – 2

9. In complex W $(CO)_n$ $(NO)_m$ which value of n and m will follow $18e^{\Theta}$.
   (a) n = 0, m = 4   (b) m = 0, n = 6
   (c) $n \neq m \neq 0$, n = 3, m = 2   (d) all of these.

10. In complex (C_6H_6) Cr $(Co)_4$ follows 18 e^{Θ} rule then haptacity of C_6H_6 will be.

(a) 5 (b) 6 (c) 4 (d) 8

11. Identify the first row trantition metal for the following $18e^{\Theta}$ species.

(a) $[M\ (CO)_3\ (PPh_3)]^-$ (b) $[HM\ (CO)_5]$

(c) $[(\eta^4 - C_8H_8)\ M\ (CO)_3]$ (d) $[(\eta^5 - C_5H_5)\ M\ (CO)_3]_2$

12. Which of the following complexes shows $17e^{\Theta}$ species.

(a) Mn $(CO)_5$ (b) Co Cl $(CO)_4$ (c) $[Mn\ (CO)_5]^-$ (d) Cr $(CO)_6$

13. What is the oxidation state of molybdenum in $[(\eta^7$ – tropylium) Mo $(CO)_3]^+$.

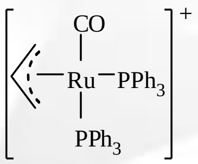
(a) + 2 (b) + 1 (c) 0 (d) – 1

14. Which of the following complex is in which organic ligand is having only bond with metal?

(a) $W(CH_3)_6$ (b) K $[PtCl_3\ (C_2H_4)]$ (c) $(\eta^5 - C_5H_5)_2$ Fe (d) $(\eta^5 - C_6H_6)_2$ Ru

15. In this complex $[M\ (CO)_7]^+$, which follows $18e^{\Theta}$ rule. Find what the unknown transition metal M.

(a) V (b) Cr (c) Mn (d) Fe

16. The complex  follows:

(a) 18 e^{Θ} rule & stable (b) 16 e^{Θ} rule & unstable

(c) 18 e^{Θ} rule & thermodynamically unstable (d) 16 e^{Θ} rule & stable

17. Using the 18 e^{Θ} rule, predict the value of n & m of the 3d-metal of the following complex.

$[(\eta^6 - C_6H_6)_nCr(CO)_m]$

(a) 2, 4 (b) 1, 3 (c) 3, 5 (d) 1, 4

18. Among the following, the unstable carbonyl species is:

(a) $[Mn(CO)_5Cl]$ (b) $[Mn(CO)_5]^-$(c) $[Mn(CO)_5]^+$ (d) $[Mn(CO)_5]$

19. An organometallic compound amongest the following is:

(a) Ferrocene (b) CaC_2 (c) tetraethyl lead (d) All of these

20. The sandwich complex $(\eta^5 - Cp)CoC_nH_n$ is an 18 e^{Θ} species where 'n' is

(a) 6 (b) 4 (c) 3 (d) 5

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ANSWER KEY

1. (b)	11.(c)
2. (c)	12.(a)
3. (b)	13.(c)
4. (b)	14.(a)
5. (c)	15.(a)
6. (d)	16.(d)
7. (a)	17.(b)
8. (a)	18.(d)
9. (d)	19.(a)
10.(c)	20.(b)

HINTS & SOLUTION

1. **Sol.** Cr= $6e^{\Theta}$

Cp= $5e^{\Theta}$

NO = $3e^{\Theta}$

$(CO)_2$=

if there is no mention of structure of NO then we consider it linear in which it donate $3e^{\Theta}$.

Correct option is (b)

2. **Sol.** $[Fe\,(CO)_4]^{2-}$= 8 + 8 + 2 = $18e^{\Theta}$

$[(\eta^5 - C_5H_5)_2\,CO]^+$= 10 + 9 – 1 = $18e^{\Theta}$

$[Ir\,(pph_3)_2\,COCl]$= 9 + 4 + 2 + 1 = $16e^{\Theta}$

$[\eta^3 - C_5H_5)\,(\eta^5 - C_5H_5)\,Fe\,(CO)]$ = 3 + 5 + 8 + 2 = $18e^{\Theta}$

Option (c) does not follow $18e^{\Theta}$ rule.

3. **Sol.** 6 + 1 + 1 + 2 – 1 + M= $18e^{\Theta}$

10 + M = $18e^{\Theta}$

M = $8e^{\Theta}$

Ru option (b) is correct.

4. **Sol.** Mo = $6e^{\Theta}$

$\left(\begin{matrix} P: \\ \\ P: \end{matrix}\right. = 4e^{\Theta}$

$H - C \equiv C \Rightarrow$

We add $7e^{\Theta}$ which make it $18e^{\Theta}$

So, $7e^{\Theta}$ will be tropylium ion.

Correct option is (b).

5. **Sol.** η + 6 + 4 = $18e^{\Theta}$

η= 18 – 10

= $8e^{\Theta}$

So, η will 3 and 5

Option (c) is correct.

6. **Sol.** Cp Fe $(CO)_2$= 5 + 8 + 4 = $17e^{\Theta}$

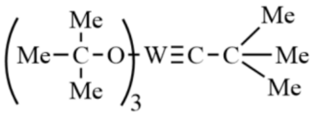
CpMo $(CO)_3$ = 5 + 6 + 6 = $17e^{\Theta}$

Cp_2 Co = 10 + 9 = $19e^{\Theta}$

Cp_2 Ru = 10 + 8 = $18e^{\Theta}$

Correct option is (d).

7. **Sol.**



Canbyne formal charge = – 3

$(Me_3\ CO)_3$ formal charge = – 3

$$C = M + L$$
$$O = M - 3 - 3$$
$$= M - 6$$
$$M = +6$$
$$W = +6$$

Option (a) is correct.

8. **Sol.**$[\eta^5\ Cp\ (CO)_2\ Fe\ (Ph - C \equiv C - H)]^Z$

$$5 + 4 + 8 + 2 + Z = 18e^{\Theta}$$
$$19e^{\Theta} + Z = 18e^{\Theta}$$
$$Z = 18 - 19e^{\Theta}$$
$$= -1e^{\Theta}$$

So in this complex $1e^{\Theta}$ is more so we substract $1e^{\Theta}$ then + 1 will be charge.

Option (a) is correct.

9. Sol. (a) $n = 0\ W(CO)_O\ (NO)_m = W\ (NO)_m$

$= W\ (NO)_4$

$= 6 + 12$

$= 18e^{\Theta}$

(b) $m = 0\ W(CO)_n\ (NO)_o = W\ (CO)n$

$= W\ (CO)_6$

$= 6 + 12 = 18e^{\Theta}$

(c) $n \neq m \neq 0\ W(CO)_3\ (NO)_2 = 6 + 6 + 6$

$= 18e^{\Theta}$

All Option are correct.

10. **Sol.** η–$(C_6H_6) + 6 + 8$

$4 + 14 = 18e^{\Theta}$

So, haptacity is η^4

option (c) is correct.

11. **Sol.**(a)$[M\ (CO)_3\ PPh_3]^-$

$$3CO = 6$$
$$PPh_3 = 2$$
$$1e^{\Theta} = \frac{1}{9}$$

$9e^{\Theta}$ for M, So metal is CO

(b) $[H\ M\ (CO)_5]$

$5\,CO = 10$

$H = \frac{1}{11}$

$7e^{\Theta}$ for M, So metal is Mn

(c) $[(\eta^4 - C_8H_8)\ M\ (CO)_3]$

$3CO = 6$

$\eta^4 - C_8H_8 = \frac{4}{10}$

$8e^{\Theta}$ for M So metal is Fe

(d) $[(\eta^5 - C_5H_5)\ M\ (CO)_3]_2$

$3CO = 6$

$\eta^5 - (C_5H_5) = 5$

$M - M = \frac{1}{12}$

$6e^{\Theta}$ for M, So metal is Cr

So, option (c) is correct.

12. **Sol.**In the tromoleptic carbonyle complexes metal having odd no. of electrons does not followed $18e^{\Theta}$ rule.

$Mn\ (CO)_5 = 7 + 10 = 17e^{\Theta}$

$Co\ Cl\ (CO)_4 = 9 + 8 + 1 = 18e^{\Theta}$

$[Mn\ (CO)^5]^- = 7 + 10 + 1 = 18e^{\Theta}$

$Co\ (CO)_6 = 6 + 12 = 18e^{\Theta}$

Correct option is (a).

13. **Sol.** C= M + L

1 = Mo + 0 + 1

1 = Mo + 1

Mo = 1 – 1 = 0.

14. **Sol.**$CH_3$is the only σ donor ligand.

While C_2H_4, C_5H_5, C_6H_5 are π-acceptor ligands.

Option (a) is correct.

15. **Sol.** $[M\ (CO)_7]^+ = 18e^{\Theta}$

$M + 14 - 1 = 18e^{\Theta}$

$M + 13 = 18e^{\Theta}$

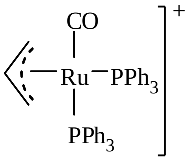
$M = 18 - 13$

$= 5e^{\Theta}$

The unknown metal is vanadium

Correct option is (a)

16. **Sol.**



$= 8 + 2 + 2 + 2 + 3 - 1 = 16\ e^{\Theta}$ and it is stable

So, correct option is (d)

17. **Sol.** $[(\eta^6 - C_6H_6)_nCr(CO)_m]$

$= 1 \times 6 + 6 + 2 \times 3$

$= 6 + 6 + 6$

$= 18\ e^{\Theta}\ 1$

Correct option is (b)

18. **Sol.** (a) $[Mn(CO)_5Cl] = 7 + 10 - 1 = 16\ e^{\Theta}$

(b) $[Mn(CO)_5]^{-} = 7 + 10 + 1 = 18\ e^{\Theta}$

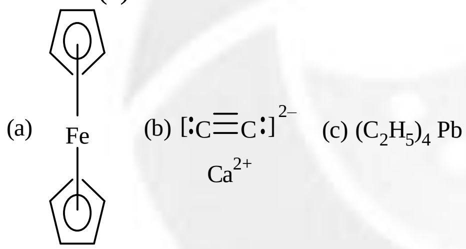
(c) $[Mn(CO)_5]^{+} = 7 + 10 - 1 = 16\ e^{\Theta}$

(d) $[Mn(CO)_5] = 7 + 10 = 17\ e^{\Theta}$

Because it is 17 e^{Θ} species which is unstable. 16 and 18 e^{Θ} species are stable.

Correct option is (d)

19. **Sol.** (a)



All of the above have M – C bond present. So it is consider as organometallic compound.

20. **Sol.** $(\eta^5 - Cp)CoC_nH_n$

$= 5 \times 1 + 9 + 4$

$= 18\ e^{\Theta}$

$n = 4$

$(\eta^5 - Cp)\ Co(C_4H_4)$

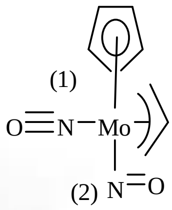
Correct option is (b)

DPP – (2) OMC

1. In complex (η^5 – C_5Me_5) $IrMe_2$ (dmso), oxidation state of Ir is–

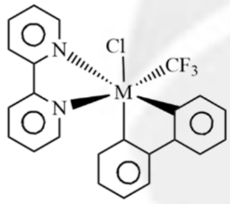
   (a) V (b) III (c) I (d) IV

2. Calculate oxidation state and electron count of the following complex



   (a) + 2, 16e$^{\ominus}$ (b) + 1, 18e$^{\ominus}$ (c) + 2, 18e$^{\ominus}$ (d) + 1, 16e$^{\ominus}$

3. Predict the oxidation state and unknown quantity of the following complex:



   (a) + 2, Ru (b) + 4, Pd (c) + 4, Pt (d) + 2, Pt

4. Which of the following complex does not satisfy the 18e$^{\ominus}$ rule?

   (a) [(η^5 C_5H_5) Ru (Cl) (CO) (PPh_3)] (b) [W $(CO)_3$ ($SiMe_3$) (Cl) $(NCMe_2)_2$]

   (c) [$IrCl_3$ $(PPh_3)_2$ ($AsPh_2$)]$^{\ominus}$ (d) [Os (N) Br_2 (PMe_3) (NMe_2)]$^{\ominus}$

5. Considering 18e$^{\ominus}$ rule, the value of Z in this complex [Co $(CO)_3$]^z will be.

   (a) – 3 (b) + 3 (c) + 2 (d) – 1

6. Nickilocene is stable in

   (a) Monocationic form (b) Dicationic form

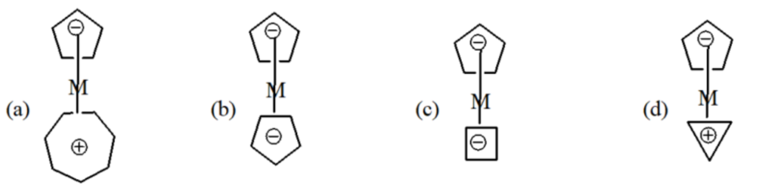
   (c) Dianionic form (d) Monoanionic form

7. Calculate the value of n if the complex follows 18e$^{\ominus}$ rule.

   [Mn Br $(CS)_n$]

   (a) 3 (b) 5 (c) 2 (d) 4

8. Select the preffered metal among these?



   (a) Mo, Ru, Ir, Ni (b) Ru, Mo, Ir, Ni (c) Ir, Mo, Ni, Ru (d) Ni, Ir, Mo, Ru

9. The highest oxidation state metal is.

(a) $Cr(\eta^6 - C_6H_6)_2$ (b) $Mn(CO)_5Br$ (c) $Na_2[Fe(CO)_4]$ (d) $K[Mn(CO)_5Br]^-$

10. The stable Cyclopentadienyl complex.
(a) $Be(Cp)_2$ (b) $Be(\eta^2 - Cp)(\eta^3 - Cp)$
(c) $[Be(\eta^1 - Cp)(\eta^3 - Cp)]$ (d) $[Be(\eta^1 - Cp)(\eta^5 - Cp)]$

11. The value of x in Fe3(CO)x is:
(a) 8 (b)9
(c)10 (d)12

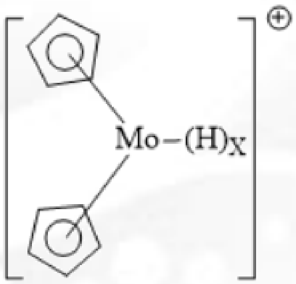
12. $[M(CO)_X]^{Z-}$ follows $18e^{\ominus}$ rule then what will be value of M, X and Z

	M	X	Z
(a)	Ti	6	1
(b)	V	6	1
(c)	Co	4	2
(d)	Mo	5	1

13. What are oxidation states of metal ion following complexes?
(I) $PdCl_2$ (II) $Pd(PPh_3)_4$ (c) $Pd(OAc)_2$ (d) ArPdBr (Ar = Aryl)
(a) 2, 4, 2, 2 (b) 2, 0, 2, 1 (c) 2, 0, 2, 2 (d) 0, 0, 0, 2

14. Which of the following complexes show easy oxidation?
(a) $(\eta^5 - C_5H_5)_2Fe$ (b) $(\eta^5 - C_5H_5)_2Ru$ (c) $(\eta^5 - C_5H_5)_2Co$ (d) $[\eta^5 - C_5H_5)_2Co]^+$

15. Predict the value of X and Oxidation state of the following complex.



(a) 3, + 6 (b) 3, + 2 (c) 2, + 2 (d) 2, + 6

16. The hapticity of nitrosyl $[Mo(\eta^1\ allyl)_3(\eta^3\ allyl)_2NO]$ is:
(a) 1 (b) 2 (c) 3 (d) 0

17. To satisfy the 18 $e^{\ominus}$ rule in the complex [Cycloheptatriene,$Mo(CO)_3$], the hapticity of the coordinated Cycloheptatriene ligand must be:
(a) 6 (b) 5 (c) 4 (d) 2

18. Oxidation number of Fe in $[Fe(NO)(CN)_5]^{2-}$ is:
(a) 1 (b) 2 (c) 3 (d) 0

19. Which of the following is not an organometallic compound.
(a) Ethyl magnesium bromide (b) Tetraethyl lead
(c) Sodium ethoxide (d) Trimethyl aluminium

20. Which second row transition metal is present in the following compound:
$(\eta^5 - C_5H_5)(Cis\text{-}\eta^4 - C_4H_6)M(PMe_3)(H)$
(a) Zr (b) Nb (c) Mo (d) Ru

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ANSWER KEY

1. (b)
2. (c)
3. (c)
4. (d)
5. (a)
6. (b)
7. (b)
8. (a)
9 (b)
10.(d)
11. (d)
12. (b)
13. (c)
14. (c)
15. (a)
16. (a)
17. (a)
18. (b)
19.(c)
20.(c)

HINTS & SOLUTION

1. **Sol.** C = M + L — C = Charge
formal charge of Me = – 1 — M = Oxidation state
formal charge of (η^5 – C_5 Me_5) = – 1 — L = formal charge of ligand.

C = M + L
O = Ir – 3
Ir = + 3

Correct option is (b)

2. **Sol.** Oxidation state:

1. NO (Linear) + 1
2. NO (bent) = – 1

(η^5 – C_5H_5) = – 1
(η^3 – C_3H_5) = – 1

C = M + L
O =
= Mo – 2
Mo = + 2

Electron count:

η^5 – C_5H_5 = $5e^{\Theta}$
η^3 – C_3H_5 = $3e^{\Theta}$
NO (Linear) = $3e^{\Theta}$
NO (bent) = $1e^{\Theta}$
Mo =

Correct option is (c)

3. **Sol.** Oxidation state

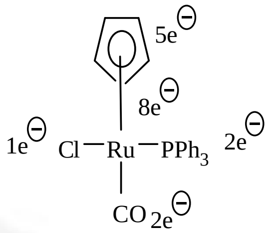
Cl = –1
CF_3 =
C = M + L
O = M – 4
M = + 4

electron count

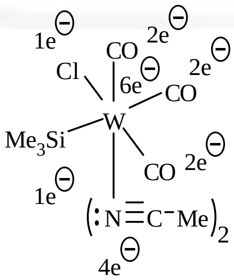
Cl = $1e^{\Theta}$
CF_3 =
x + 8 = $18e^{\Theta}$
x = 18 – 8
= $10e^{\Theta}$
= d^{10}
Pt = d^{10}

Option (c) is correct.

4. **Sol.** (a)

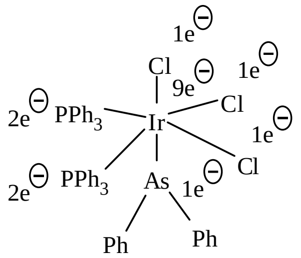


= 5 + 8 + 2 + 2 + 1 = 18e$^{\ominus}$



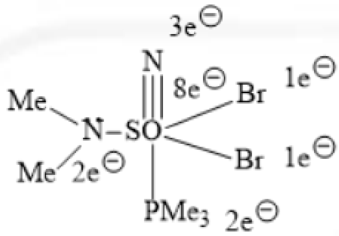
= 6 + 2 + 2 + 2 + 2 + 2 + 1 + 1 = 18e$^{\ominus}$

(b)



$= 9 + 1 + 1 + 1 + 1 + 1 + 2 + 2 + 1 = 18e^{\ominus}$

(c)
(d)



$= 8 + 3 + 2 + 2 + 1 + 1 = 17e^{\Theta}$.

Option (d) does not follow $18e^{\Theta}$ rule.

5. **Sol.** $[Co\,(CO)_3]^Z = 18e^{\Theta}$

$9 + 6 + Z = 18e^{\Theta}$

$15 + Z = 18e^{\Theta}$

$Z = 18e^{\Theta} - 15e^{\Theta}$

$= 3e^{\Theta}$

in this complex we add $3e^{\Theta}$ so the value of Z is – 3.
Option (a) is correct.

6. **Sol.** $[Cp_2\,Ni] \rightarrow [Cp_2\,Ni]^{2+}$

$10 + 10 = 20e^{\Theta}$ $\quad$ $10 + 10 - 2 = 18e^{\Theta}$

So in dicationic form it will obey $18e^{\Theta}$.
Correct option is (b)

7. **Sol.** CS Just like CO = $2e^{\Theta}$ donar

$[Mn\,Br\,(CS)_n] = 18e^{\Theta}$

$7 + 1 + 2n = 18e^{\Theta}$

$8 + 2n = 18e^{\Theta}$

$2n = 18 - 8$

$2n = 10e^{\Theta}$

$n = \frac{\cancel{10}}{\cancel{2}}\ 5e^{\ominus}$

$n = 5e^{\Theta}$

So, Correct option is (b)

8. **Sol.**(a) $6 + 7 = 13 + 6$ = Mo
(b) $5 + 5 = 10 + 8$ = Ru
(c) $5 + 4 = 9 + 9$ = Ir
(d) $5 + 3 = 8 + 10$ = Ni
Correct option is (a)

9. **Sol.** $Cr\,(\eta^6 - C_6H_6)_2 = Cr + 0 = Cr = 0$

$Mn(CO)_5Br = Mn + 0 - 1 = Mn = +1$

$Na_2[Fe(CO)_4] = Fe + 0 = -2 = Fe = -2$

$K^+[Mn(CO)_5Br]^-$ $= Mn + 0 - 1 = -1, Mn = -1 + 1 = 0$

10. **Sol.**(a) $Be(Cp)_2 = 2 + 10 = 12e^{\Theta}$

(b) $Be(\eta^2 - Cp)(\eta^3 - Cp) = 2 + 2 + 3 = 7e^{\Theta}$

(c) $[Be(\eta^1 - Cp)(\eta^3 - Cp)] = 2 + 1 + 3 = 6e^{\Theta}$

(d) $[Be(\eta^1 - Cp)(\eta^5 - Cp)] = 2 + 1 + 5 = 8e^{\Theta}$

Option (d) is correct.

11. **Sol.** (d)12

12. **Sol.** $[M(CO)_X]^{Z-}$

$[V(CO)_6]^-$

$5 + 12 + 1 = 18e^{\Theta}$

Option (b) is correct.

13. **Sol.**(a) $PdCl_2 \rightarrow \begin{matrix} L = M + L \\ 0 = Pd - 2 \\ Pd = +2 \end{matrix}$

(b) $Pd(PPh_3)_4 \rightarrow \begin{matrix} C = M + L \\ 0 = M + 0 \\ Pd = 0 \end{matrix}$ (PPh_3 = neutral ligand)

(c) $Pd(OAC)_2 \rightarrow \begin{matrix} C = M + L \\ 0 = Pd - 2 \\ Pd = +2 \end{matrix}$

(d) $ArPdBr \rightarrow \begin{matrix} C = M + L \\ 0 = Pd - 1 - 1 \\ 0 = Pd - 2 \\ Pd = +2 \end{matrix}$

Option (c) is correct.

14. **Sol.**(a) $(\eta^5 - C_5H_5)_2Fe = 8 + 10 = 18e^{\Theta}$

(b) $(\eta^5 - C_5H_5)_2Ru = 8 + 10 = 18e^{\Theta}$

(c) $(\eta^5 - C_5H_5)_2Co = 9 + 10 = 19e^{\Theta}$

(d) $(\eta^5 - C_5H_5)_2Co^+ = 9 + 5 + 5 - 1 = 18e^{\Theta}$

Since in $(\eta^5 - C_5H_5)_2Co$ one e^{Θ} extra of stable no., oxidation $\rightarrow$ there is lose of e^{Θ} can take place easily.

So, option (c) is correct.

15. **Sol.** Value of X $\rightarrow$ 2 (Cp) + Mo + x (H) – 1 = 18

10 + 6 + x (H) – 1 = 18

$15 + x(H) = 18e^{\Theta}$

x (H) = 18 – 15

$x = 3e^{\Theta}$

Oxidation state $\rightarrow$ 2 (Cp) + Mo + 3 (H) = 1

– 2 + Mo – 3 = 1

$Mo - 5 = 1$
$Mo = 1 + 5$
$= +6$

Correct option is (a)

16. **Sol.** $[Mo(\eta^1\text{-allyl})_3(\eta^3\text{-allyl})_2NO]$

$= 6 + 3 + 6 + 1 = 16\ e^{\Theta}$

Hapticity of nitrosyl = η^1

Correct option is (a)

17. **Sol.**[Cycloheptatriene,$Mo(CO)_3$]

$= 6 + 6 + 3 \times 2$

$= 6 + 6 + 6$

$= 18\ e^{\Theta}$

Correct option is (a)

18. **Sol.** $[Fe(NO)(CN)_5]^{2-}$

TVE = 8 + 3 + 5 + 2

$= 18\ e^{\Theta}$

Here NO is in linear form charge of NO is + 1

O.S. $= Fe + 1 - 5 = -2$
$= Fe - 4 = -2$
$= Fe = -2 + 4 = +2$

Correct option is (b)

19. **Sol.** In this M – C bond is not present

Correct option is (c)

20. **Sol.** $(\eta^5 - C_5H_5)$ (Cis-$\eta^4 - C_4H_6$)$M(PMe_3)(H)$

$= 5 + 4 + M + 2 + 1 = 18\ e^{\Theta}$

$= 12 + M = 18\ e^{\Theta}$

$M = 18 - 12 = 6\ e^{\Theta}$

M = Mo

Correct option is (c)

QUANTA CHEMISTRY

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DPP- 03 ONCE

1. What is the total electron count and geometry of the given complex. $[Rh_9P(CO)_{21}]^{2-}$
   (a) 128, trigonal prism (b) 130, trigonal prism
   (c) 130, capped square anti prismatic (d) 129, square Anti-prismatic
2. Calculate the per M – M bond in the given complex
   $$[\mu - X - \mu - CH_2\,[Os_3(CO)_{10}]^-$$
   (a) 1 (b) 2 (c) 0 (d) 3
3. Consider the following molecule and assign its structure / geometry
   $Os_6(CO)_{17}[P(OMe)_3]_3$
   (a) Closo, Octahedral (b) Nido, Octahedral
   (c) Nido, Pentagonal bipyramid (d) Closo, pentagonal bipyramid
4. Determine the unknown quantity of the given complex $[(Cp)_3Ni_3(\mu_3 - CO)_2]^z$ having 3 Ni – Ni bond.
   (a) – 1 (b) + 2 (c) + 1 (d) – 2
5. Calculate the per M – M bond in the given complex –
   $(CO)_4V\,(\mu - PR_2)_2V(CO)_4$
   (a) 3 (b) 2 (c) 1 (d) 0
6. In the given complex, $[(\eta^2 - \text{ethylene})_2Rh(\mu - H)]_2$ the geometry around Rhodium is square planar, determine the expected bond order of the Rh-Rh bond.
   (a) 1 (b) 3 (c) 2 (d) 0
7. The number of skeletal electrons present in the compounds $C_2B_3H_5$, $C_2B_4H_6$ and B_5H_9 are, respectively
   (a) 10, 12 and 12 (b) 12, 14 and 14 (c) 10, 12 and 14 (d) 12, 14 and 12
8. The complex $[M(\eta^6 - C_6H_6)\,(CO)_2]_2$ obeys the 18 e^- – rule and has M = M, then predict the metal present in it.
   (a) Fe (b) Cr (c) Rh (d) V
9. Classify the structure of the given complex $[PCB_9H_{11}]^-$
   (a) Closo (b) Nido (c) Arachno (d) Klado

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10. Predict the shape of the following complex given

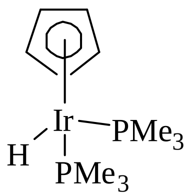
$Fe_4C(CO)_{13}$

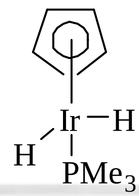
(a) Closo (b) Arachno (c) Nido (d) Hyper closo

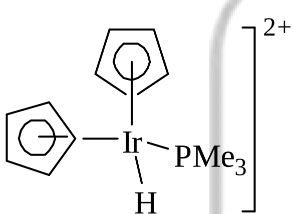
11. Assuming that the 18 e^- – rule is followed predict the number of M – M bonds in the given complex $[Mn(\mu - PH_2)(CO)_4]_3$

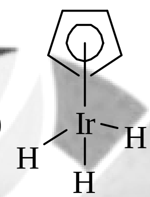
(a) 1 (b) 2 (c) 0 (d) 3

12. Draw a possible 18 e^- structural formed by the combination of given metal and ligand Ir, Cp, H, PMe_3

(a) 

(b) 

(c) 

(d) 

13. Predict the number of per M – M bond in the given complex

$(\mu - CO) - [\eta^5 - CpRe(CO)_2]_2$

(a) 2 (b) 1 (c) 0 (d) 3

14. Predict the number of per M – M bond in the given complex

$(\mu^3 - CO) - [Fe_4(CO)_{12}]^{2-}$

(a) 3 (b) 2 (c) 6 (d) 1

15. $Os_6(CO)_{18}$ has monocapped TBP structure. Upon adding two electrons, the structure changes to octahedral. What will be the structures of both complexes according to wade's rule.

(a) Closo to hyper chloso (b) Nido to closo

(c) Closo to nido (d) hyper closo to closo

16. Predict the shape of the given complex

$SiC_2B_4H_{10}$

(a) Nido (b) Arachno (c) closo (d) hyper closo

17 . If in complex $[(\eta^5 - Cp)\ Mn(CO)_X]_2$, the number of M – M are two, x is

(a) 1 (b) 4 (c) 3 (d) None of these

18. Total number of M – M bonds in $(\mu - C_2H_2)OS_2(CO)_6$

(a) 2 (b) 3 (c) 1 (d) None of these

19. The oxidation state of Ni and the number of M–M bonds in $[Ni_2(CO)_6]^{2-}$ that are consistent with 18e$^-$–rule are

(a) Ni^{2-}, 1 bond (b) Ni^{4+}, 2 bonds
(c) Ni^{-}, 1 bond (d) Ni^{4+}, 3 bonds

20. The structure of $OS_3 (CO)_{12}$ is
(a) Closo (b) Nido
(c) Arachno (d) Super Hyper closo

21. The structure of $[Re_7C(CO)_{21}]^{3-}$ is
(a) Nido (b) Closo (c) Arachno (d) Capped closo

22. Total number of M—M bonds in
$(\mu - CH_2)_2$—$[Cp^*Rh(CH_3)]_2$
(a) 2 (b) 3 (c) 1 (d) 0

23. Structure of a carborane with formula, $C_2B_4H_8$ is formally derived from
(a) Closo-borane (b) Nido-Borane
(c) Arachno Borane (d) Conjuncto-Borane

24. Predict the metal-metal bonds in the given complex $(\mu - Br)_2$–$[Mn(CO)_4]_2$
(a) 1 (b) 0 (c) 2 (d) 3

25. Predict the no. of M—M bonds in the given complex— μ—CO—μ—$CH_2[\eta^5$—$CpRh]_2$
(a) 1 (b) 0 (c) 2 (d) 3

26. Predict the no. of M—M bonds of the given complex $(\eta^5 - C_5H_5)(CO)Fe(\mu\text{–}CO)_2Fe(CO)(\eta^5\text{–}C_5H_5)$
(a) 2 (b) 1 (c) 0 (d) 3

27. Classify the structure of the given complex $C_2B_3H_7$
(a) Closo (b) Arachno
(c) Nido (d) Klado

28. Classify the structure of the given complex $[SB_{10}H_{10}]^{2-}$
(a) Closo (b) Nido
(c) Arachno (d) Super closo

29. Classify the structure of the given complex— $As_2C_2B_7H_9$
(a) Closo (b) Nido (c) Arachno (d) Hypercloso

30. Metal–Metal Quadruple bonds are well known for the metal.
(a) Ni (b) Co (c) Fe (d) Re

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ANSWERS

1.	c	11.	c	21.	d
2.	c	12.	b	22.	c
3.	c	13.	b	23.	b
4.	c	14.	a	24.	b
5.	b	15.	d	25.	c
6.	c	16.	b	26.	b
7.	b	17.	d	27.	c
8.	b	18.	a	28.	b
9	b	19.	c	29.	b
10.	b	20.	c	30.	d

HINT & SOLUTIONS

1. c

Sol. TEC $= 9 \times 9 + 5 + 21 \times 2 + 2$

$= 81 + 5 + 42 + 2$

$= 130\ e^-$

$\therefore$ It's geometry is capped square anti-prismatic

2. c

Sol. '0' / can't determine

TEC $= 3 + 2 + 8 \times 3 + 2 \times 10 + 1 \quad (\because\ \mu - x = 3)$

$= 50\ e^-$

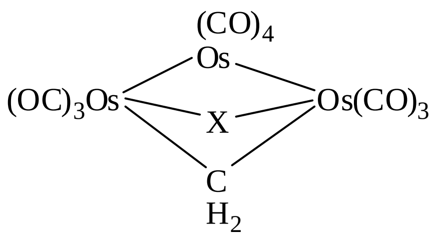
$$\therefore \text{ per M – M bond } = 18 - \frac{\text{TEC}}{\text{Total no. of metals}}$$

$$= 18 - \frac{50}{3}$$

= Fraction

We can't determine the exact number of per M – M bonds of this complex.

The structure of the complex will is



3. c

Sol. TEC $= 6 \times 8 + 17 \times 2 + 2 \times 3$

$= 48 + 34 + 6$

$= 88\ e^-$

PEC $= \text{TEC} - 12 \times n$

$= 88 - 12 \times 6$

$= 88 - 72$

$= 16\ e^-$

$$\frac{\text{PEC}}{2} = \frac{16}{2} = 8 \text{ pairs}$$

i.e. (n + 2) Nido

(6 + 2)

4. c

Sol. TEC $= 3 \times 5 + 3 \times 10 + 2 \times 2 + z = 18 \times 3$

$\Rightarrow 15 + 30 + 4 + z + 6 = 54$

$$\left(\because 3\underset{\substack{\downarrow \\ 6e^-}}{\text{M}} - \text{Mbonds}\right)$$

$\Rightarrow 6 + 49 + z = 54$

$z = 54 - 55$

$z = -1$

As we known the sign of the charge taken is opposite to the observed one

$\therefore$ the ans will be + 1 i.e. option 'c'

5. b

Sol. TEC $= 4 \times 2 + 5 + 2 \times 3 + 5 + 4 \times 2$

$= 8 + 5 + 6 + 5 + 8$

$= 32\ e^-$

per M – M bonds $= 18 - \dfrac{\text{TEC}}{n}$

$$= 18 - \frac{32}{2}$$

$$= 18 - 16$$

$$= 2$$

6. c

Sol. TEC $= (2 \times 2 + 9 + 1) \times 2$

$= 14 \times 2$

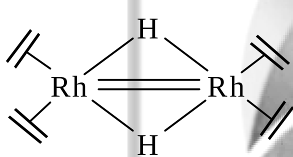
$= 28\ e^-$

M – M bond $= \frac{16 \times n - TEC}{2}$

$$= \frac{16 \times 2 - 28}{2}$$

$$= \frac{32 - 28}{2}$$

$$= \frac{4}{2} = 2$$

Structure 

7. b

Sol. (a) $C_2B_3H_5 \leftrightarrow (BH)_2B_3H_5$

$= (B_5H_5)H_2$

$= 5 \times 2 + 2$

$= 12\ e^-$

(b) $C_2B_4H_6 \leftrightarrow (BH)_2B_4H_6$

$= (B_6H_6)H_2$

$= 6 \times 2 + 2$

$= 14\ e^-$

(c) $B_5H_9 \leftrightarrow (BH)_5H_4$

$= 5 \times 2 + 4$

$= 14\ e^-$

8. b

Sol. TEC of the complex obeying 18 e^- – rule is

$4 + (M + 6 + 2 \times 2) \times 2 = 36$ (4 due to M = M)

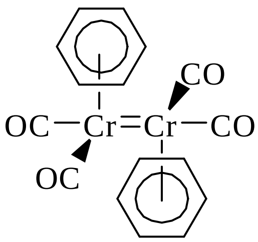
$2M + 24 = 36$

$2M = 36 - 24$

2 M = 12

$M = \frac{12}{2} = 6$

$\therefore$ we have Cr | Mo | w metal taking palce:

structure 

9 ‘b’

Sol. $\left[PCB_9H_{11}\right]^- \leftrightarrow \left[(BH_2)(BH)B_9H_{11}\right]^-$ $(\because P = BH_2 \text{ unit})$

$= \left[(BH)_{11} H_3\right]^-$ or $[B_{11}H_{11}]^{4-}$ uinit (Nido)

$= \frac{11 \times 2 + 3 + 1}{2}$

$= \frac{22 + 4}{2}$

$= \frac{26}{2} = 13$ i.e. $\underset{(11+2)}{\underset{\downarrow}{(n+2)}}(\text{Nido})$

10. b

Sol. $Fe_4C(CO)_{13}$ electron count is

TEC $= 4 \times 8 + 4 + 13 \times 2$

$= 32 + 4 + 26$

$= 62\ e^-$

PEC $= 62 - 12 \times 4$

$= 62 - 48$

$= 14$

$\frac{PEC}{2} = \frac{14}{2} = 7$

i.e. $\underset{(4+3)}{\underset{\downarrow}{(n+3)}}$ Arachano

11. c

Sol. TEC $= 7 \times 3 + 3 \times 3 + 2 \times 12$

= 21 + 9 + 24

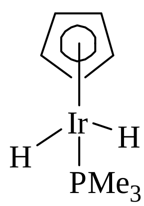
= 54 e^-

M – M bond $= \frac{18 \times 3 - 54}{2}$

$= \frac{54 - 54}{2} = 0$

There is no. M – M bond in this complex.

12. b

Sol. 

obeys 1f e^-

9 + 5 + 1 + 1 + 2 = 18 e^-

13. b

Sol. TEC = 2 + (5 + 7 + 2 × 2) 2

= 2 + 16 × 2

= 34 e^-

per M – M bond $= 18 - \frac{TEC}{n}$

$= 18 - \frac{34}{2}$

= 18 – 17

= 1

14. a

Sol. TEC = 2 + 4 × 8 + 12 × 2 + 2

= 2 + 32 + 24 + 2

= 60 e^-

per M – M bond $= 18 - \frac{60}{4}$

= 18 – 15

= 3

15. d

Sol. $Os_6(CO)_{18}$ electron count will be

= 6 × 8 + 18 × 2

= 48 + 36

= 84 e^-

PEC = 84 – 12 × 6

$= 84 - 72$

$= 12$

$\frac{PEC}{2} = \frac{12}{2} = 6$ i.e. (n) (hyper closo)

and when we add $2e^-$ complex become

$[Os_6(CO)_{18}]^{2-}$ and TEC = 86

$\therefore$ PEC = 86 – 72 = 14

$= \frac{PEC}{2} \frac{14}{2} = 7$ i.e. (n + 1) closo (6 + 1)

16. b

Sol. $SiC_2B_4H_{10} \leftrightarrow (BH)(BH)_2B_4H_{10}$ $\quad (\because Si = BH\,unit)$

$= (BH)_7H_6$

$= \frac{7 \times 2 + 6}{3}$

$= \frac{14 + 6}{2}$

$= \frac{20}{2} = 10$ i.e. (n + 3)

Arachno (7 + 3)

17. (d)

Sol. TEC = 5 × 2 + 7 × 2 + 2 × 2 × x + 4 = 18 × 2

$\Rightarrow$ 10 + 14 + 4x + 4 = 36

28 + 4x = 36

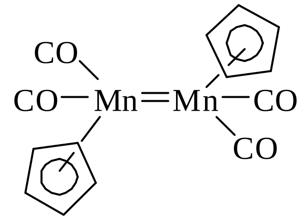
4x = 36 – 28

4x = 8

x = 2

$\left(\begin{array}{c} Mn = Mn \\ \downarrow \\ \text{e–count} = 4 \end{array} \right)$

$\therefore$ The complex will become



18. (a)

Sol. To find M – M bond we have,

$$\text{M – M bond} = \frac{18\times n - \text{TEC}}{2}$$

$\therefore$ TEC = 8 × 2 + 6 × 2 + 2 × 2 = 16 + 12 + 4 = 32e$^-$

$$\text{Now, M – M bond} = \frac{18\times 2 - 32}{2} \Rightarrow \frac{36-32}{2} = \frac{4}{2} = 2.$$

19. (c)

Sol. Oxidation state of $[Ni_2(CO)_6]^{2-}$ is

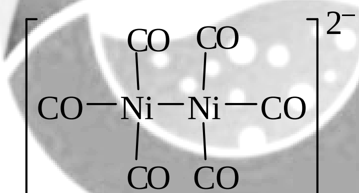
$$2x + 0 = -2$$
$$x = -1$$

$$\text{Now, M—M bond} = \frac{18\times n - \text{TEC}}{2}$$

TEC = 10 × 2 + 6 × 2 + 2 = 20 + 12 + 2 = 34e$^-$

$$\therefore \quad \text{M—M bond} = \frac{18\times 2 - 34}{2} = \frac{36-34}{2} = \frac{\cancel{2}^1}{\cancel{2}} = \boxed{1}$$

$\therefore$ The structure will be—



20. (c)

Sol.
TEC = 8 × 3 + 12 × 2
= 24 + 24
= 48e$^-$ (14n + 6)
PEC = TEC – 12 × n
= 48 – 12 × 3
= 48 – 36
= 12

$$\frac{\text{PEC}}{2} = \frac{12}{2} = 6 \ (n + 3) \text{ i.e. } (3 + 3)$$

$\therefore$ $OS_3(CO)_{12}$ is Arachno metal cluster.

21. (d)

Sol. TEC = 7 × 7 + 4 + 21 × 2 + 3

$= 49 + 4 + 42 + 3$

$= 98e^-$

$PEC = TEC - 12 \times n$

$= 98 - 12 \times 7$

$= 98 - 84$

$= 14$

$$\frac{PEC}{2} = \frac{14}{2} = 7\ (n)$$

A $98e^-$, seven metal cluster is two electrons short of a closo configuration. The structure would be expected to be capped closo or hyper closo.

22. (c)

Sol. $TEC = 5 \times 2 + 9 \times 2 + 1 \times 2 + 2 \times 2$

$= 10 + 18 + 2 + 4$

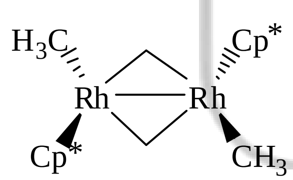
$= 34e^-$

$$\therefore \quad M—M \text{ bond} = \frac{18 \times n - TEC}{2}$$

$$= \frac{18 \times 2 - 34}{2}$$

$$= \frac{36 - 34}{2} = \frac{2}{2} = \boxed{1}$$

$\therefore$ The structure will become



23. (b)

Sol. We can write C_2 as $(BH)_2$ unit

$\therefore$ $C_2B_4H_8$ becomes $(B_2H_2B_4H_8)$

No. of skeletal electron pairs $= B_6H_{10}$

$= (BH)_6H_4$ or $[B_6H_6]^{4-}$ (Nido)

$$= \frac{6 \times 2 + 4}{2}$$

$$= \frac{12+4}{2} = \frac{16}{2} = 8 \text{ i.e. } (6+2) \rightarrow (n+2) \text{ Nido}$$

24. (b)

Sol. TEC = $7 \times 2 + 4 \times 2 \times 2 + 3 \times 2$ (μ_2-Br = 3)

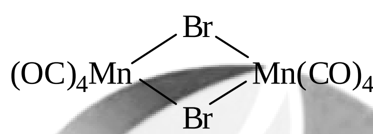
$= 14 + 16 + 6$

$= 36e^-$

$\therefore$ M—M bond = $\frac{18 \times 2 - 36}{2}$

$= \frac{36-36}{2} = \boxed{0}$

There is no M—M bond b/w Mn which means the structure will be



25. (c)

Sol. TEC = $2 + 2 + 5 \times 2 + 9 \times 2$

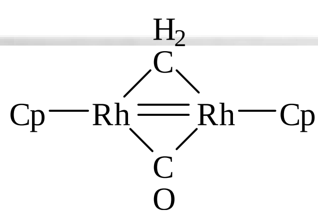
$= 4 + 10 + 18$

$= 32e^-$

M—M bonds = $\frac{18 \times n - \text{TEC}}{2}$

$= \frac{18 \times 2 - 32}{2} = \frac{36-32}{2} = \frac{4}{2} = \mathbf{2}.$

$\therefore$ Structure becomes,



26. (b)

Sol. TEC = $5 + 2 + 8 + 2 \times 2 + 8 + 2 + 5$

$= 34e^-$

M—M bonds = $\frac{18 \times n - \text{TEC}}{2}$

$\Rightarrow \frac{18 \times 2 - 34}{2} = \frac{36-34}{2} = \frac{2}{2} = 1$

27. (c)

Sol. $C_2B_3H_7 \longleftrightarrow (BH)_2B_3H_7 (\because \quad C = BH \text{ unit})$

$= (B_5H_5)H_4 \text{ or } (B_5H_5)^{4-}$ (Nido)

$$= \frac{5 \times 2 + 4}{2}$$

$$= \frac{10 + 4}{2}$$

$$= \frac{14}{2} = \mathbf{7\ pairs}$$

i.e., (n + 2) (5 + 2) Nido

28. (b)

Sol. $[SB_{10}H_{10}]^{2-} \longleftrightarrow [BH_3B_{10}H_{10}]^{2-} (\because \quad S = BH_3)$

$= [(BH)_{11}H_2]^{2-}$

or $(B_{11}H_{11})^{4-}$ (Nido)

$$= \frac{11 \times 2 + 2 + 2}{2}$$

$$= \frac{26}{2}$$

= 13 pairs i.e. (n + 2) (11 + 2) Nido

29. (b)

Sol. $As_2C_2B_7H_9 \longleftrightarrow (BH_2)_2(BH)_2B_7H_9$

$= (BH)_{11}H_4$ or $(B_{11}H_{11})^{4-}$ (Nido)

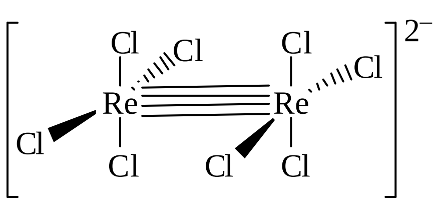
= T

$$= \frac{22 + 4}{2} = \frac{26}{2} = 13 \text{ pairs}$$

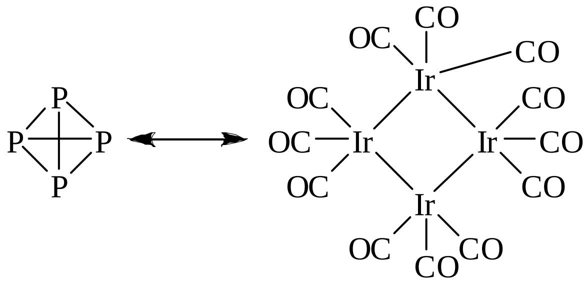
i.e. (n + 2) (11 + 2) Nido

30. (d)

Sol. Example $[Re_2Cl_8]^{2-}$



The Quadruple Re—Re bond is made of one σ-bond two π-bonds and one δ-bond.l.



$$\text{TEC} = 9 \times 4 + 12 \times 2$$
$$= 36 + 24$$
$$= 60 \ (14n + 4)$$
$$\text{PEC} = 60 - 12 \times 4 = 12$$

$$\frac{\text{PEC}}{2} = \frac{12}{2} = 6 \text{ i.e. } (4 + 2) \text{ i.e. } (n + 2) \text{ Nido}$$

$$= B_6H_{10}$$
$$= (BH)_6H_4$$
$$= \frac{6 \times 2 + 4}{2}$$
$$= \frac{12 + 4}{2}$$
$$= \frac{16}{2} = 8 \text{ i.e. } (6 + 2) \rightarrow (n + 2) \text{ Nido}$$

QUANTA CHEMISTRY

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DPP- 04 OMC

1. Which of the following cluster have highest symmetrical point group.

(a) $[B_5H_9]$ (b) $[C_2B_4H_7]$ (c) $[B_{12}H_{12}]^{2-}$ (d) $[B_{10}H_{16}]$

2. The number of isomer for $C_2B_{10}H_{12}$ are:

(a) 3 (b) 2 (c) 4 (d) none of these

3. Calculate the number of skeletal electrons present in the $[C_2B_4H_6]$, $[B_6H_6]^{2-}$ and $[B_5H_5]^{2-}$ are respectively:

(a) 12, 14, 14 (b) 14, 12, 14 (c) 14, 14, 12 (d) None of these

4. The number of available frame work e^{Θ} of $[B_6H_6]^{2-}$ is:

(a) 7 (b) 6 (c) 4 (d) 5

5. Calculate the total number of vertices in metal clusters $[Rh_6(CO)_{16}]$, $[Os_5(C)(CO)_{15}]$ and $[Ru_5(C)(CO)_{16}]$ respectively are:

(a) 5, 6, 5 (b) 6, 5, 5 (c) 5, 5, 6 (d) None of these

6. Predict the structure and geometry of the complex $C_2B_3H_5$ respectively.

(a) Nido, square pyramidal (b) Closo, trigonal bipyramidal

(c) Nido, trigonal bipyramidal (d) Closo, square pyramidal

7. The intense band at 15000 cm^{-1} in UV-visible spectrum of $[Bu_4N]_2Re_2Cl_8$ is due to transition.

(a) $\pi - \pi^*$ (b) $\delta - \delta^*$ (c) $\delta - \pi^*$ (d) $\pi - \delta^*$

8. The molecular orbital configuration of the Re–Re bond in $[Re_2Cl_8]^{2-}$ is:

(a) $\sigma^2\ \pi^4\ \delta^2\ \delta^{*1}$ (b) $\sigma^2\ \pi^2\ \delta^2\ \delta^{*2}$ (c) $\sigma^2\ \pi^2\ \delta^2\ \pi^{*2}$ (d) $\sigma^2\ \pi^4\ \delta^2$

9. Geometry involved in $[Re_2Cl_8]^{2-}$

(a) Tetrahedral (b) Square planar (c) Square pyramidal (d) none of these

10. The number of metal-metal bond present in $[Re_2Cl_8]^{2-}$ is

(a) 2 (b) 4 (c) 3 (d) 5

11. Geometry involved in $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_8]^{4-}$ respectively are:

(a) Eclipsed, Eclipsed (b) staggered, eclipsed

(c) Eclipsed, staggered (d) staggered, staggered

12. The M–M bond and magnetic nature of $[Re_2Cl_8]^{2-}$ respectively are:

(a) Quadruple bond, paramagnetic (b) Triple bond, diamagnetic

(c) Triple bond, paramagnetic (d) quadruple bond, diamagnetic

13. Considering the quadruple nature of M–M bond in $[Re_2Cl_8]^{2-}$, the M–M bond order in $[Mo_2(HPO_4)_4]^{2-}$, $[Re_2Cl_4(PMe_2Ph)_4]^{+}$, $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$ and $[Os_2Cl_8]^{2-}$ respectively are.

(a) 3, 3.5, 4, 3 (b) 3, 4, 3.5, 3 (c) 4, 3.5, 3, 3 (d) 4, 3, 3, 3.5

14. Zintl ion Bi_5^{3+} is cluster of:

(a) closo (b) Nido (c) Arachno (d) Hypho

15. Addition of two electrons of the bismuth cluster Bi_5^{3+} results in a change of structure type from

(a) closo to nido (b) nido to arachno (c) closo to arachno (d) arachno to hypho

16. Predict the structure of the following zintl's ions:

(a) $In_4Bi_5^{3-}$ (b) $Pb_2Fe_3Cr_2(CO)_{19}^{2-}$ (c) $Tl_2Te_2^{2-}$ (d) $Pb_2Sb_2^{2-}$

(e) $Ga_3R_3^{2-}$

17. Geometry of $[Ge_9]^{3-}$ is

(a) Tricapped trigonal prismatic (b) Bicapped square antiprismatic

(c) Monocapped square antiprism (d) none of these

18. Find out the structure of the following complexes.

(a) $B_3H_7\,[Fe(CO)_3]_2$ (b) $C_2B_4H_6Pt(PEt_3)_2$

(c) $C_2B_7H_7Me_2Fe(CO)_3$ (d) CB_9H_{10} As (CoCP)

(e) $Co(\eta^5\text{–}C_5H_5)B_4H_8]$ (f) $[Mn(\eta^2\text{–}B_3H_8)(CO)_4]$

19. In the cluster $[Co_3(CH)(CO)_9]$ obeying $18e^{\Theta}$ rule, the number of M–M bonds and the bridging ligands respectively are:

(a) 3 and 1 CH (b) 0 and 3 CO (c) 3 and 1 CO (d) 6 and 1 CH

20. Among the following, the correct statement is:

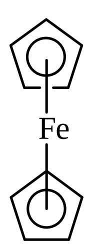
(a) CH is isolobal to $Co(CO)_3$ (b) CH_2 is isolobal to $Ni(CO)_2$

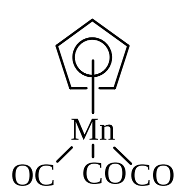
(c) CH is isolobal to $Fe(CO)_4$ (d) CH_2 is isolobal to $Mn(CO)_4$

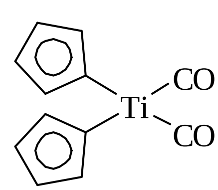
21. Which of the following metal fragments, d^9–MLn is isolobal with CH?

(a) $d^7\text{–}ML_5$ (b) $d^8\text{–}ML_4$ (c) $d^9\text{–}ML_3$ (d) $d^5\text{–}ML_6$

22. Which of the following complexes are isolobal with each other?

(a) 

(b) 

(c) 

(d) All of these

23. The complex $Mn(CO)_5$ is replaced by-

(a) CH_2 (b) CH_3 (c) CH (d) SiR_2

24. Which of the following Boranes is isolobal with the complex $Me_2C_2B_{10}H_{10}$:

(a) B_5H_9 (b) $B_{12}H_{12}^{2-}$ (c) B_4H_{10} (d) $B_6H_6^{4-}$

25. Among the following the correct statement is:

(a) $[Os_5(CO)_{15}]^{2-}$ is isolobal with $[B_5H_5]^{2-}$

(b) $[Os_6(CO)_{15}]^{2-}$ is isolobal with $[B_5H_5]^{2-}$

(c) $[Os_5(CO)_{15}]^{2-}$ is isolobal with $[B_{12}H_{12}]^{2-}$

(d) $[Os_6(CO)_{15}]^{2-}$ is isolobal with $[B_{12}H_{12}]^{2-}$

26. Determine the number of skeletal electron pair of the given complex.

$(\eta^5\text{–}C_5H_5)CoB_4H_{10}$

(a) 7 (b) 14 (c) 12 (d) 8

27. Classify the main group cluster by structural type, $[Ge_9]^{4-}$

(c) Closo (b) Nido (c) Arachno (d) Klado

28. What will be the bond order and geometry of the given inorganic cluster compound

$[Os_2Cl_8]^{2-}$

(a) 3, Eclipsed (b) 3.5, Eclipsed (c) 3, Staggered (d) 3.5, staggered

29. Match up the total valence electron count with the metal core shape. Which one is incorrect?

(a) 48 e^-, trimer

(b) 74 e^-, trigonal bipyramidal

(c) 86 e^-, octahedron

(d) 90 e^-, trigonal prism

30. For which cluster is the stated structure for the metal core incorrect with the cluster electron count.

(a) $Os_3(CO)_{12}Br_2$, trimer (b) $Rh_4(CO)_{12}$, tetrahedron

(c) $[Os_6(CO)_{18}]^{2-}$ octahedron (c) $[Rh_6(CO)_{16}]$, octahedron

31. Octahedral fragment of formula ML_n i.e. $Fe(CO)_4$ is isolobal with which fragment

(a) $[PtCl_3]^-$ (b) $Pt(PR_3)_2$ (c) $[PtCl_4]^{2-}$ (d) None of these

32. Find organic fragments isolobal with $[Fe(CO)_2(PPh_3)]^-$

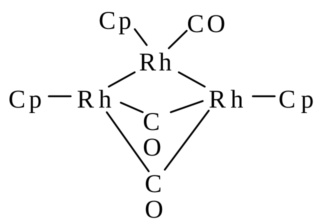
(a) CH (b) CH_3^+ (c) CH_2 (d) CH_2^+

33. Classify the given metallaboranes by structural type.

$C_2B_4H_6\ Ni(PPh_3)_2$

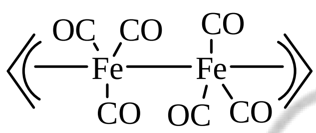
(a) Closo (b) Nido (c) Arachno (d) Super closo

34. Describe the isolobal organic hydrocarbon fragment for the given molecule.



(a) CH (b) CH_2 (c) CH_3^+ (d) CH_2^+

35. Predict the isolobal fragment for the given molecule/complex.



(a) CH_3–CH_3 (b) HC_2–CH_2 (c) CH–CH (d) None of these

36. Classify the following

In Bi_3^{2-}

(a) Closo (b) Nido (c) Archano (d) Super closo

37. Classify the structure of the given compound.

$C_2B_9H_{11}Ru(CO)_3$

(a) Nido (b) Closo (c) Arachno (d) Super closo

38. CO coordinates most strongly with metals of zero oxidation state primarily due to

(a) Trans effect (b) The necessity of following EAN rule.

(b) The intensive polarity of th CO molecule (d) An increased opportunity for π-bonding.

39. Classify the structure of the given complex

$B_3H_8Mn(CO)_3$

(a) Closo (b) Nido (c) Arachno (d) Super closo

40. Choose the isoelectronic pair among the following.

(A) $[V(CO)_6]$ (B) $[Cu(\eta^5–C_5H_5)(CO)]$

(C) $[Co(CO)_4]^-$ (D) $[IrCl(CO)(PPh_3)_2]$

(a) A and B (b) B and C (c) C and D (d) A and D

××××××

ANSWERS

1.(c)	12.(d)	23.(b)	34.(b)
2.(a)	13.(a)	24.(b)	35.(a)
3.(c)	14.(a)	25.(a)	36.(b)
4.(a)	15.(a)	26.(d)	37.(b)
5.(b)	16.(a)	27.(b)	38.(d)
6.(b)	17.(a)	28.(c)	39.(b)
7.(b)	18.(a)	29.(b)	40.(b)
8.(d)	19.(a)	30.(a)	
9.(b)	20.(a)	31.(b)	
10.(b)	21.(c)	32.(a)	
11.(c)	22.(d)	33.(a)	

HINT & SOLUTIONS

1. (c)

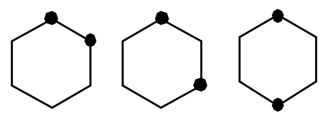
Sol. $[B_2H_{12}]^{2-}$ have highest symmetrical point group it has icosahedral geometry.

$[B_{12}H_{12}]^{2-}$ = closo = icosahedral geometry

Correct option is (c)

2. (a)

Sol. $C_2B_{10}H_{12} \longrightarrow [(BH)_2B_{10}H_{12}] \longrightarrow [B_{12}H_{14}] \xrightarrow{-2H^+} [B_{12}H_{12}]^{2-} \longrightarrow$ Icosahedral



Ortho Meta Para

Number of isomers are three.

Correct option is (a).

3. (c)

Sol. $[C_2B_4H_6] = [(BH)_2B_4H_6] = [B_6H_8] = [B_6H_6]^{2-}$

= 6 BH + 2

= 6 × 2 + 2

= 14

$[B_6H_6]^{2-}$ = 6BH + 2

= 6 × 2 + 2

= 12 + 2

= 14

$[B_5H_5]^{2-}$ = 5BH + 2

= 5 × 2 + 2

= 10 + 2

= 12

Correct option is (c)

4. (a)

Sol. $[B_6H_6]^{2-}$

= 6BH + 2

= 6 × 2 + 2

= 12 + 2

= 14

$= \frac{14}{2} = 7e^{\Theta}$

Correct option is (a)

(e) $[Ru(CO)_3]$

5. (b)

Sol. $Rh_6(CO)_{16}$ = 6 × 9 + 16 × 2 = 86.

Number of skeletal electron pair $= \frac{1}{2}[86 - 6 \times 12]$

= 7

= (6 + 1) = closo.

Number of vertices = n – 1

= 7 – 1

= 6

$[Os_5(C)(CO)_{15}]$ = 5 × 8 + 4 + 15 × 2 = 74

Number of skeletal electron pair $= \frac{1}{2}[74 - 5 \times 12]$

= 7

= (5 + 2) = nido

Numer of vertices = n – 2

= 7 – 2

= 5

$[Ru_5(C)(CO)_{15}]$ = 5 × 8 + 4 + 15 × 2 = 74

Number of skeletal e^{Θ} pairs $= \frac{1}{2}[74 - 5 \times 12]$

$= \frac{14}{2} = 7$

= (n + 2) = (5 + 2) = nido.

Number of vertices = n – 2 = 7 – 2 = 5

Correct option is (b)

6. (b)

Sol. $C_2B_3H_5$

$(BH)_2B_3H_5$

B_5H_7

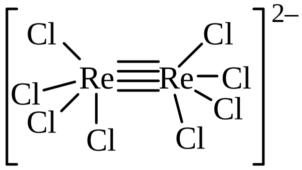
$[B_5H_5]^{2-}$

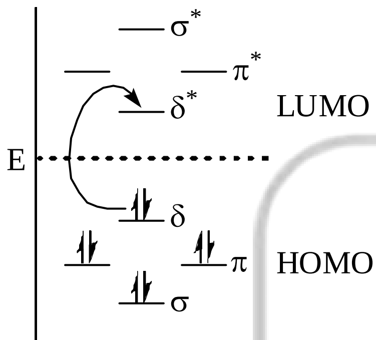
Closo

n = 5, trigonal bipyramidal.

7. (b)

Sol. $[Bu_4N]_2\ Re_2Cl_8 \longrightarrow 2[Bu_4N]^+ + [Re_2Cl_8]^{2-}$





Spectrum is due to δ–δ^* transition.

Correct option is (b)

8. (d)

Sol.

$[Re_2Cl_8]^{2-}$

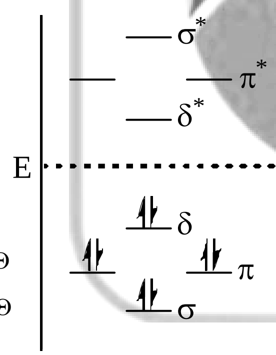
C = M + L

$-2 = 2x - 8$

$2x = +6$

$2Re(0) = 14e^{\Theta}$

$2Re(+6) = 8e^{\Theta}$



$\sigma^2\pi^4\delta^2$

Correct option is (d)

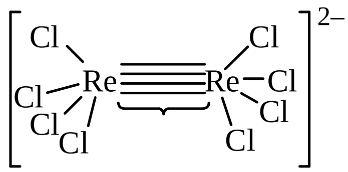
9. (b)

Sol. In $[Re_2Cl_8]^{2-}$, M-L bond shows dsp^2 hybridisation in which $d_{x^2-y^2} + s + p_x + p_y$ orbitals are involved. So geometry will be square planar.

Correct option is (b)

10. (b)

Sol. The number of M–M bond present in $[Re_2Cl_8]^{2-}$ is 4.



$$\left.\begin{matrix}1\sigma\\2\pi\\1\delta\end{matrix}\right\}\text{—M—M bond}$$

11. (c)

Sol. $[Re_2Cl_8]^{2-}$

$2Re^{3+} = d^4$

$2 \times Re^{3+}\ (d^4) = 8e^{\Theta}$

$(\sigma)^2(\pi)^4(\delta)^2$

bond order = 4 (quadruple bond)

δ-bond = eclipsed geometry

$[Re_2Cl_8]^{4-}$

$2Re^{2+} = d^5$

$2 \times Re^{2+}\ (d^5) = 10e^{\Theta}$

$(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$

bond order = 3 (triple bond)

δ-bond = staggered geometry.

Correct option is (c)

12. (d)

Sol. All e^{Θ} are paired so diamagnetic, and M–M bond = 4

$[Re_2Cl_8]^{2-}$

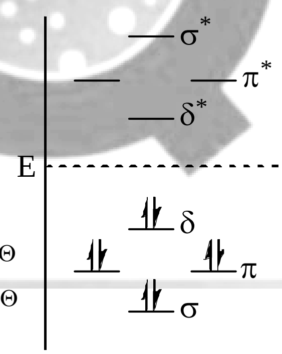
C = M + L

$-2 = 2x - 8$

$2x = +6$

$2Re(0) = 14e^{\Theta}$

$2Re(+6) = 8e^{\Theta}$



Correct option is (d)

13. (a)

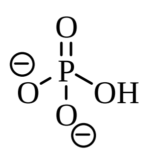
Sol. $[Mo_2(HPO_4)_4]^{2-}$

C = M + L

$-2 = 2x - 8$

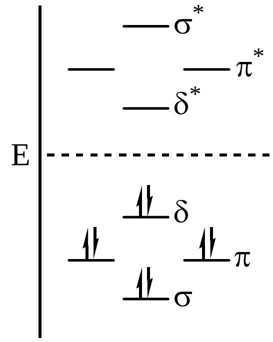
$2x = +6$

$2Mo(0) = 12e^{\Theta}$



$2Mo(+6) = 12 - 6 = 6e^{\ominus}$

$$B.O. \frac{6-0}{2} = \frac{6}{2} = 3$$



$[Re_2Cl_4(PMe_2Ph)_4]^+$

C = M + L

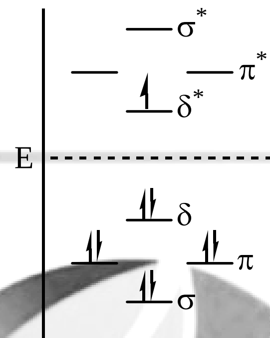
1 = 2x – 4

2x = 5

$2Re(0) = 14e^{\ominus}$

2Re(+5) = 14 – 5

= 9



$$B.O. \frac{8-1}{e} = \frac{7}{2} = 3.5$$

$[Re_2Cl_4(PMe_2Ph)_4]^{2+}$

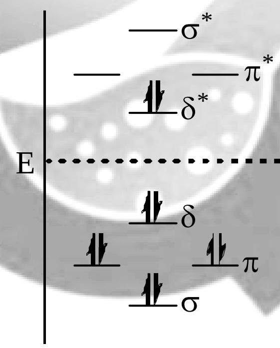
C = M + L

2 = 2x – 4

2x = +6

2Re(0) = 14

2Re(+6) = 14–6 = 8



$$B.O. = \frac{8-0}{2} = \frac{4}{2} = 4$$

$[Os_2Cl_8]^{2-}$

C = M + L

–2 = 2x – 8

2x = –2 + 8

2x = + 6

$2Os(0) = 16e^{\ominus}$

2Os(+6) = 16–6

$= 10\ e^{\ominus}$

$$B.O. = \frac{8-0}{2} = \frac{6}{2} = 3$$

Correct option is (a)

14. (a)

Sol. $(Bi_5)^{3+} = 5 \times 5 - 3 = 22$

$(4n + 2) = (4 \times 5 \times 2) = 22$

Closo

Correct option is (a)

15. (a)

Sol. $Bi_5^{3+} \xrightarrow{2e^{\ominus}} Bi_5^{+}$

Closo Nido

$5 \times 3 - 3 = 22$ $(5 \times 5 - 1) = 24$

$(4 \times 5 + 2) = 22$ $4 \times 5 + 4 = 24$

Correct option is (a)

16. (a)

Sol. $In_4Bi_5^{3-} = 5 \times 5 + 3 \times 4 + 3$

$= 25 + 12 + 3$

$= 40$

$n = 9 = (4n + 4)$

$= 4 \times 9 + 4$

$= 40$ (Nido)

(b) $Pb_2Fe_3Cr_2(CO)_{19}^{2-} = (4n + 6)$

$= 4 \times 7 + 6$

$n = 7 = 28 + 6$

$= 34$ (Arachno)

(c) $Tl_2Te_2^{2-}$

$= 4 \times 4 + 2$

$n = 4 = 16 + 2$

$= 18$ (Closo)

(d) $Pb_2Sb_2^{2-} = 4n + 4$

$n = 4 = 4 \times 4 + 4$

$= 16 + 4 = 20$ (Nido)

(e) $Ga_3R_3^{2-} = 4n + 2$

$n = 3 = 4 \times 3 + 2 = 14$ (Closo)

17. (a)

Sol. $[M_9]^{3-}$ = Tricapped trigonal prismatic where M = Si, Ge, Sn.

Correct option is (a)

18. (a)

Sol. $B_3H_7[Fe(CO)_3]_2$

$Fe(CO)_3 = 8 + 6 = 14e^{\ominus}$

$14e^{\ominus} \longleftrightarrow 4e^{\ominus} \longleftrightarrow C \longleftrightarrow BH$

$Fe(CO)_3 \longleftrightarrow BH$

$B_3H_7\,[BH]_2$

$B_5H_9 = [B_5H_5]^{4-}$ = Nido

(b) $C_2B_4H_6Pt\,(PEt_3)_2$

$Pt(PEt_3)_2 = 10 + 4 = 14e^{\ominus}$

$14e^{\ominus} \longleftrightarrow C \longleftrightarrow BH$

$(BH)_2B_4H_6(BH)$

$B_6H_8(BH)$

B_7H_9

$[B_7H_7]^{2-}$ = Nido

(c) $C_2B_7H_7Me_2\,Fe(CO)_3$

$Fe(CO)_3 = 8 + 6 = 14e^{\ominus}$

$14e^{\ominus} \longleftrightarrow C \longleftrightarrow BH$

$Me \longleftrightarrow CH_3 \longleftrightarrow H$

$(BH)_2B_7H_7\,(H)_2\,(BH)$

$B_{10}H_{12} = [B_{10}H_{10}]^{2-}$ = closo

(d) CB_9H_{10}

As (CoCP) $As \longleftrightarrow BH_2$

$(BH)B_9H_{10}BH_2(BH)$ $CoCp = 9 + 5 = 14e^{\ominus}$.

$14e^{\ominus} \longleftrightarrow C \longleftrightarrow BH$

$B_{12}H_{14} = [B_{12}H_{12}]^{2-}$ = closo.

(e) $[Co(\eta^5{-}C_5H_5)B_4H_8]$

$Co[\eta^5{-}C_5H_5] = 9 + 5 = 14$

$14e^{\ominus} \longleftrightarrow C \longleftrightarrow BH$

$(BH)B_4H_8$

$B_5H_9 = [B_5H_5]^{4-}$ = nido

$[Mn(\eta^2\text{–}B_3H_8)\,(CO)_4]$

$Mn(CO)_4 = 7 + 8 = 15e^{\Theta}$

$15e^{\ominus} \longleftrightarrow N \longleftrightarrow BH_2$

$(BH_2)\,(B_3H_8)$

$B_4H_{10} = [B_4H_4]^{6-}$ = Arachno.

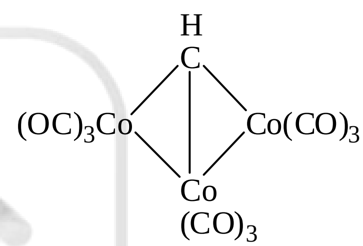
19. (a)

Sol. $[Co_3(CH)(CO)_9]$

TEC = $9 \times 3 + 3 + 18$

$= 27 + 21$

$= 48e^{\Theta}$



1CH contribute '$3e^-$'

So, it will distribute $3e^{\Theta}$ in 3 Co.

M–M bond $= \dfrac{18 \times 3 - 48}{2}$

$= \dfrac{54 - 48}{2} = \dfrac{6}{2} = 3$

Correct option is (a).

20. (a)

Sol. CH = 4 + 1 = 5

$Co(CO)_3$ = 9 + 6 = 15

$CH \longleftrightarrow Co(CO)_3$

CH is isolobal to $Co(CO)_3$

Correct option is (a)

21. (c)

Sol. $d^9 – ML_3$

$9 + 3 \times 2$

$d^9\text{–}ML_3 \longleftrightarrow CH$

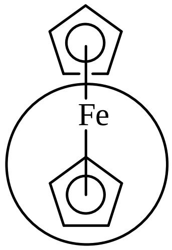
9 + 6

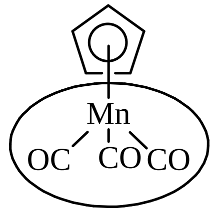
15

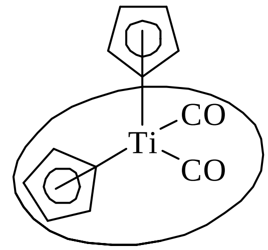
CH = 4 + 1 = 5

Correct option is (c)

22. (d)

Sol. (a) 

(b) 

(c) 

Cp+Fe = 8 + 5 = $13e^{\Theta}$ $Mn(CO)_3$ = 7 + 6 = $13e^{\Theta}$ $CpTi(CO)_2$ = 5 + 4 + 4 = $13e^{\Theta}$

all are isolobal.

Correct option is (d)

23. (b)

Sol. $Mn(CO)_5 = 7 + 10 = 17e^{\Theta}$

$Mn(CO)_5 \longleftrightarrow CH_3$

$CH_3 = 4 + 3 = 7e^{\Theta}$

$17e^{\Theta} \longleftrightarrow 7e^{\Theta}$

Correct option is (b).

24. (b)

Sol. $Me_2C_2B_{10}H_{10}$

$(H)_2(BH)_2B_{10}H_{10}$

$B_2H_4B_{10}H_{10}$

$B_{12}H_{14}$

$[B_{12}H_{12}]^{2-}$ = closo, structure $\rightarrow$ Icosahedral

Correct option is (b)

25. (a)

Sol. $[Os_5(CO)_{15}]^{2-} = \dfrac{72-5\times12}{2} = \dfrac{12}{2} = 6$

= (n + 1) = closo = (5 + 1) = closo

If the structure is same then it will be isolobal.

Correct option is (a).

26. (d)

Sol. $(\eta^5-C_5H_5)Co \xleftrightarrow{\text{Isolobal}}$ BH

$5+9=14e^-$ $3+1=4e^-$

$\therefore$ complex become BHB_4H_{10}

$\Rightarrow B_5H_{11} = (BH)_5H_6 \quad = \frac{5\times2+6}{2} \quad = \frac{10+6}{2} \quad = \frac{16}{2} = 8$ pairs

Correct option is (d)

27. (b)

Sol. $Ge_9^{4-} = 9\times4+4$

$= 36 + 4$

$= 40$ i.e. $(4 \times 9 + 4) \rightarrow (4n + 4)$ Nido

Correct option is (b)

28. (c)

Sol. Let the O.S. of the two O.S. atoms are x and y.

$x + y - 8 = -2$

$x + y = -2 + 8$

$x + y = +6$

$\therefore\ x = +3 \qquad y = +3$

i.e. $Os^{3+} = 5d^5$ $Os^{3+} = 5d^5$

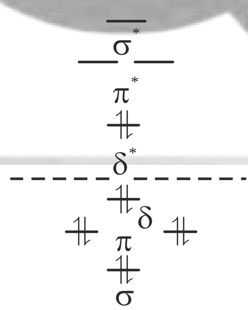
Therefore, total number of d-electrons on Os^{3+} are

$5 + 5 = 10$

Electronic configuration in this cluster ion is $\sigma^2\pi^4\delta^2\delta^{*2}$

Bond order $= \frac{8-2}{2} = \frac{6}{2} = 3$

and have staggered geometry.



Correct option is (c)

29. (b)

Sol. 74 e^- count have square pyramid geometry.

Correct option is (b)

30. (a)

Sol. $Os_3(CO)_{12}\,Br_2$ have TEC

$= 3 + 8 + 2 \times 12 + 2 = 24 + 24 + 2 = 50\ e^-$

$\therefore$ it does not follows correct total electron count having geometry trimer.

The geometry for 50 e^- count is acyclic trimer.

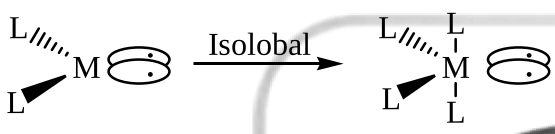
Correct option is (a)

31. (b)

Sol. Octahedral fragments $\xleftrightarrow{\text{Isolobal}}$ Square planer fragments

ML_n $\qquad\qquad$ ML_{n-2}

$$\therefore \begin{array}{ccc} Fe(CO)_4 & \xleftrightarrow{\text{Isolobal}} & Pt\ (PR_3)_2 \\ d^8 & & d^{10} \end{array}$$



$Pt(PR_3)_2$ $\qquad\qquad$ $Fe(CO)_4$

Correct option is (b)

32. (a)

Sol. $[Fe(CO)_2(PPh_3)]^- \xleftrightarrow{\text{Isolobal}} CH$

$8 + 2 \times 2 + 2 + 1$ $\qquad$ $4 + 1 = 5e^-$

$= 15e^-$

Correct option is (a)

33. (a)

Sol. $Ni\ (PPh_3)_2 \xleftrightarrow{\text{Isolobal}} BH$

$10 + 4 = 14\ e^-$ $\qquad$ $3 + 1 = 4e^-$

$\therefore C_2B_4H_6\ Ni\ (PPh_3)_2$ becomes $(BH)_2B_4H_6BH$

$\Rightarrow$ $[B_7H_9] = (BH)_7\ H_2$ $\qquad$ or $[B_7H_7]^{2-}$ unit (Closo)

$$= \frac{7 \times 2 + 2}{2} = \frac{14 + 2}{2} = \frac{16}{2} = 8 \text{ pairs}$$

i.e. (n + 1) closo $\rightarrow$ (7 + 1)

Correct option is (a)

34. (b)

Sol. Rh Cp CO = 9 + 5 + 2

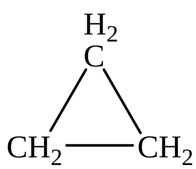
= 16 e^-

Which is isolobal with 6 e^- species

$\because$ CH_2 have 6 e^-

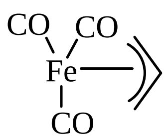
Correct option is (b)

Can also be represented as



35. (a)

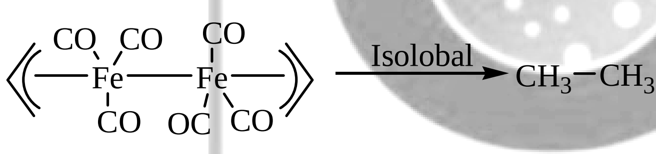
Sol.



= 8 + 3 × 2 + 3 = 17 e^-

which is isolobal with 7 e^- species.

$\therefore$ CH_3 = 3 + 4 = 7 e^-



Correct option is (a)

36. (b)

Sol. In Bi_3^{2-} = 3 + 3 × 5 + 2

= 3 + 15 + 2

= 20 e^- i.e. (4n + 4) Nido

Correct option is (b)

37. (b)

Sol.

$$\begin{array}{ccc} Ru(CO)_3 & \longleftrightarrow & \text{BH unit} \\ 8+3\times 2 = 14e^- & & 3+1 = 4\ e^- \end{array}$$

$\therefore$ The complex become.

$C_2B_9H_{11}Ru(CO)_3 = (BH)_2\ B_9H_{11}BH$

$= B_{12}H_{14}$ or $[B_{12}H_{12}]^{2-}$ unit (Closo)

$= (BH)_{12}H_2$

$$= \frac{12 \times 2 + 2}{2} = \frac{26}{2} = 13 \text{ i.e. } (n + 1) \text{ closo } (12 + 1)$$

Correct option is (b)

38. (d)

Sol. The reason is back bonding.

Greater the back bonding, greater will be the M–C bond strength and frequency. And π-back bonding will occur when metal is electron rich (low oxidation state).

Correct option is (d)

39. (b)

Sol. $Mn(CO)_3 \longleftrightarrow$ B unit

$7 + 3 \times 2 = 13\, e^-$ $\quad 3\, e^-$

$\therefore$ The complex become

$B_3H_8Mn(CO)_3 = B_3H_8B$

$= B_4H_8$ or $[B_4H_4]^{4-}$ unit (Nido)

$= (BH)_4H_4$

$$= \frac{4 \times 2 + 4}{2} = \frac{8 + 4}{2} = \frac{12}{2} = 6 \text{ pairs}$$

i.e., (n + 2) Nido $\rightarrow$ (4 + 2)

Correct option is (b)

40. (b)

Sol. (A) TEC of $TV[(CO)_6] = 5 + 6 \times 2 = 5 + 12 = 17\, e^-$

(B) $[Cu(\eta^5\text{– }C_5H_5)\,(CO)] = 11 + 5 + 2 = 18\, e^-$

(C) $[Co(CO)_4]^- = 9 + 4 \times 2 + 1 = 9 + 8 + 1 = 18\, e^-$

(D) $[IrCl(CO)\,(PPh_3)_2] = 9 + 1 + 2 \times 2 + 2 = 16\, e^-$

$\therefore$ B and C are isoelectronic having 18 e^-.

Correct option is (b)

××××××

DPP - 05 METAL CARBONYLS

1. CO can donate electron density and accept back through which orbitals respectively.

   (a) σ, π (b) σ^*, π (c) σ, π^* (b) σ^*, π^*

2. What will be the correct order of CO stretching frequency in $[Fe(CO)_6]^{2+}$ and free CO.

   (a) $[Fe(CO)_6]^{2+} > CO$ (b) $CO > [Fe(CO)_6]^{2+}$ (c) $[Fe(CO)_6]^{2+} = CO$ (d) None of these

3. What will be the effect on CO stretching frequency when it act as a bridging ligand.

   (a) decreases (b) increases (c) No effect (d) None of these

4. Comment on the C – O strecthing frequency.

   $Mn(CO)_{10} + Na \longrightarrow$ (A)

   $Mn_2(CO)_{10} + Br_2 \longrightarrow$ (B)

   (a) A > B (b) B > A (c) A = B (d) Can't determine.

5. The tendency of CO to bridge transition metals at going down the group gets

   (a) increases (b) decreases (c) No effect (d) None of these

6. The compound $[W(O)\,Cl_2(CO)\,(PMePh_2)_2]$ has ν (CO) 2006 cm^{-1}. Predict the ν_{CO} for $[W(S)\,Cl_2(CO)\,(PMePh_2)_2]$ to be at higher of lower energy.

   (a) higher than 2006 cm^{-1} (b) lower than 2006 cm^{-1}

   (c) same, 2006 cm^{-1} (d) None of these

7. Three such cations are $[Hg(CO)_2]^{2+}$, $[Pt(CO)_4]^{2+}$, and $[Os\,(CO)_6]^{2+}$. Predict which of these has the lowest energy carbon-oxygen stretching vibration.

   (a) $[Hg(CO)_2]^{2+}$ (b) $[Pt(CO)_4]^{2+}$

   (c) $[OS(CO)_6]^{2+}$ (d) Both 'a' and 'b' are same.

8. Match the following frequencies given with the right carbonyl complex.

Complex	ν_{CO}
(i) $P(p\text{ - }C_6H_4F)_3$	(P) 1923 cm^{-1}
(ii) $P(p\text{ - }C_6H_4Me)_3$	(Q) 1965 cm^{-1}
(iii) $P(t\text{ - }C_4H_9)_3$	(R) 1984 cm^{-1}
(iv) $P(C_6F_5)_3$	(S) 2004 cm^{-1}

(a) (i) – R, (ii) – P, (iii) – S, (iv) – Q
(b) (i) – R, (ii) – Q, (iii) – P, (iv) – S
(c) (i) – S, (ii) – Q, (iii) – P, (iv) – R
(d) (i) – Q, (ii) – R, (iii) – P, (iv) – S

9. What will be the electron count and geometry of the given complex.
$[Fe_5C(CO)_{15}]$
(a) 74, Trigonal bipyramid
(b) 74, square pyramid
(c) 72, Trigonal bipyramid
(d) 72, square pyramid

10. M — M bond is either not possible or only weak interactions are possible when configurations in metals is
(a) $d^5 - d^5$
(b) $d^2 - d^2$
(c) $d^4 - d^4$
(d) $d^8 - d^8$

11. Correct order of chemical shift of H is for H – $Mn(CO)_5$, H – Tc $(CO)_5$ and H – Re $(CO)_5$ respectively.
(a) – 5.2, –5.7, – 6.8 ppm
(b) – 6.8, –5.7, – 5.2 ppm
(c) + 6.7, +5.7, + 5.2 ppm
(d) – 5.7, –5.2, – 6.8 ppm

12. Correct order of ν_{CO} is
(a) $[Fe(CO)_6]^{2+} > CO^+ > BH_3 - CO > [Co(CO)_4]^{-1}$
(b) $CO^+ > [Fe(CO)_6]^{2+} > BH_3 - CO > [Co(CO)_4]^{-1}$
(c) $BH_3 - CO > CO^+ > [Fe(CO)_6]^{2+} > [Co(CO)_4]^{-1}$
(d) $BH_3 - CO > [Fe(CO)_6]^{2+} > [Co(CO)_4]^{-1} > Co^+$

13. Number of bridge and terminal CO ligands in $Ir_4(CO)_{12}$ at low temperature are respectively.
(a) zero and 12
(b) 3 and 9
(c) 2 and 10
(d) 4 and 8

14. The correct order of pKa value of hydrogen in
(A) $H_2Fe(CO)_4$
(B) $H_2Ru(CO)_4$
(C) $H_2OS(CO)_4$
(a) A < B < C
(b) A > B > C
(c) A = B = C
(d) C > A > B

15. The number of bridging and terminal carbonyl in $Co_2(CO)_8$ (solution) and $Co_2(CO)_8$ (solid)
(a) In both complex, 2 bridged and 6 terminal
(b) In solution all 8 are in terminal position and in solid 2 bridged and 6 terminal
(c) In both complex all 8 CO are terminal position.
(d) In solution 2 bridged and 6 terminal CO and in solid all 8 are at terminal position.

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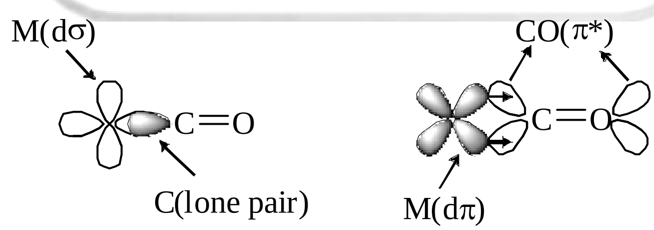
ANSWERS

1. (c)
2. (a)
3. (a)
4. (b)
5. (b)
6. (b)
7. (c)
8. (b)
9. (b)
10. (d)
11. (b)
12. (a)
13. (a)
14. (a)
15. (b)

HINT & SOLUTIONS

1. (c)

Sol. The overall effect is synergistic. CO can donate electron density via a σ-orbital to a metal atom, the greater the electron density on the metal, the more effectively it can return electron density to the π^* orbitals of CO.



CO to Mσ–donation M to CO π–donation

Correct option is (c).

2. (a)

Sol. In free CO, the electrons are polarized towards the more electronegative oxygen. For example, the electrons in the π-orbitals are concentrated nearer to the oxygen atom than to the carbon.

The presence of a transition metal cation tends to reduce the polarization in the C – O bond by attracting the bonding electrons.

$$\overset{\delta+}{C}\equiv\overset{\delta-}{O} \quad M^{n+} \longleftarrow \overset{\delta+}{C}\equiv\overset{\delta-}{O}$$

The consequence is that the electrons in the positively charged complex are more equally shared by the carbon and the oxygen, giving rise to a stronger bond and a higher energy C – O stretch.

Correct option is (a).

3. (a)

Sol. In cases in which CO bridges with metal, all metals can contribute electron density in π^* orbitals of CO to weaken the C – O bond and lower the energy of the stretch.

Correct option is (a).

4. (b)

Sol.
$$Mn(CO)_{10} + Na \longrightarrow \underset{OS=-1}{Na^+[Mn(CO)_5]^-}$$

$$Mn_2(CO)_{10} + Br_2 \longrightarrow \underset{OS=+1}{(CO)_5Mn - Br}$$

$\therefore$ Product A will have more π-back bonding due to which C — O stretching frequency decreases.

Correct option is (b).

5. (b)

Sol. Tendency of CO to bridge metals decreases in going down the periodic table, as the orbitals of bridging CO are less able to interact effectively with transition metals as the size of the metals increases.

Ans. Correct option is (b).

6. (b)

Sol. Sulfur is less electronegative than oxygen. Therefore, the tungsten in $W(S)\,Cl_2\,(PMePh_2)_2$ has greater electron density and a greater tendency to participate in π-backbonding with CO, therefore the ν_{CO} of $[W(S)\,Cl_2\,(CO)\,(PMePh_2)_2]$ is lower than $[W(O)\,Cl_2(CO)\,(PMePh_2)_2]$.

Correct option is (b).

7. (c)

Sol. As the number of carbonyl group increases, π-back bonding also increases. And hence, C – O stretching frequency decreases.

Ans. Correct option is (c).

8. (b)

Sol. Order of π-acceptor ligands.

$(C_6F_5) > (p-C_6H_4F) > (p-C_6H_4Me) > (t-C_4H_9)$

Ans. Correct option is (b).

9. (b)

Sol. TEC = 5 × 8 + 4 + 15 × 2 = 40 + 4 + 30 = $74e^-$

Hence, have square pyramid geometry.

Correct option is (b).

10. (d)

Sol. Metal–Metal bond is not possible or only weak interactions in $d^8 - d^8$ configuration.

Eg. $Ni(CO)_4$ (LNCC)

Correct option is (d).

11. (b)

Sol. In order to chemical shift, negative value decreases down the group, as the size of metal increases, overlapping or π-backbonding from metal to carbon decreases and means electron density decreases and hence less shielded protons occur.

Ans. Correct option is (b).

12. (a)

Sol. Greater the negative charge on metal greater will be π-back bonding and hence lesser will be the C – O stretching frequency,

Or, more the positive charge more will be the stretching frequency of CO.

Correct option is (a).

13. (a)

Sol. As the size of the metal increases, the tendency of bridge forming decreases. So, in $Ir_4(CO)_{12}$ there is no bridging ligand.

Correct option is (a).

14. (a)

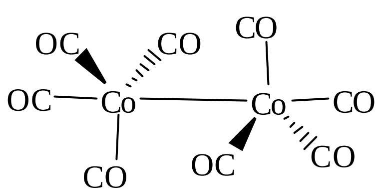
Sol. As the size increases down the group the acidic character of hydrogen decreases because CO ligand cannot effectively work as π-acceptor ligand with large size metals and hence pKa value increases.

$$\text{Size of metal} \propto \frac{1}{\text{acidic strength}} \propto \text{pKa}$$

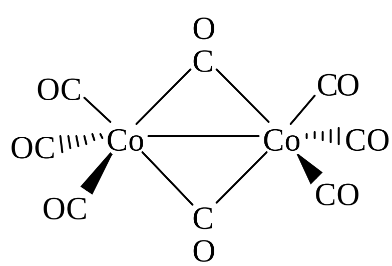
Correct option is (a).

15. (b)

Sol.



Solution



Solid

Correct option is (b).

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DPP - 06 METAL CARBONYLS

1. The electron count of linear and bent NO respectively are –
(a) 1, 3 (b) 2, 3 (c) 3, 1 (d) 2, 2

2. NO^+ is isoelectronic with which of the following
(a) PF_3 (b) CO (c) CH_4 (d) CO_2

3. Following the 18 e^- – rule as a guide, determine x in the following complex.
$[Ni(CO)_3(NO)]^x$
Considering NO as linear
(a) – 1 (b) + 2 (c) + 1 (d) – 2

4. What will be the hybridization of linear and bent nitrosyl molecule. resp.
(a) sp^2, sp (b) sp, sp^3 (c) sp, sp^2 (d) sp^2, sp^3

5. N – O bond length in $[Ru(PPh_3)_2(NO)_2Cl]^+$ is of
(a) same length (116 pm & 116 pm)
(b) different length (120 pm and 106 pm)
(c) almost same length (117 pm and 116.2 pm)
(d) different length (117 pm and 125 pm)

6. What are the types of bond involved in linear and bent mole of NO.
(a) σ and π (b) π and π (c) π and σ (d) σ and σ

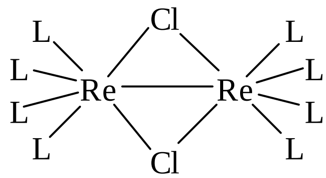
7. Considering NO as a 3e – donor, give the formula of the corresponding neutral metal carbonyls which is isoelectronic with $Fe(CO)_2(NO)_2$.
(a) $[Cr(CO)_5]^-$ (b) $Fe(CO)_5$ (c) $Ni(CO)_3$ (d) $Mn(CO)_5$

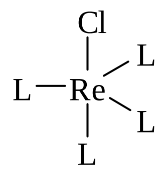
8. Match the following hydride complex with their correct chemical shifts.

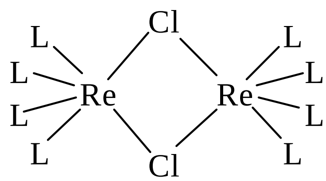
Complex	Chemical Shift
(i) $HMn(CO)_5$	(P) – 11 ppm
(ii) $H_2Fe(CO)_4$	(Q) – 7.5 ppm
(iii) $[HFe(CO)_4]^-$	(R) – 9 ppm

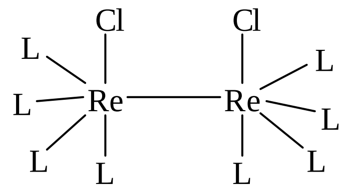
(a) (i) – P, (ii) – Q, (iii) – R (b) (i) – Q, (ii) – P, (iii) – R
(c) (i) – Q, (ii) – R (iii) – P (d) (i) – P, (ii) – R, (iii) – Q

9. The rhenium complex $Re(Cl)(N_2)(PMe_2Ph)_4$ on heating loses a colourless gas and forms a new complex. The new complex obeys the 18 e^- – rule. (L = PMe_2Ph)

(a) 

(b) 

(c) 

(d) 

10. Choose the correct increasing order of acidity of M – H bond.

(a) $HCo(CO)_3PF_3 < HCo(CO)_3P(OR)_3 < HCo(CO)_3PMe_3$

(b) $HCo(CO)_3PMe_3 < HCo(CO)_3P(OR)_3 < HCo(CO)_3PF_3$

(c) $HCo(CO)_3PMe_3 < HCo(CO)_3PF_3 < HCo(CO)_3P(OR)_3$

(d) $HCo(CO)_3P(OR)_3 < HCo(CO)_3PMe_3 < HCo(CO)_3PF_3$

11. Components of metal – dihydrogen bonding

(i) H_2 to M donation

(ii) M to H_2 donation

Using the H_2 molecular orbital respectively are:

(a) σ, σ^* (b) π, π^* (c) σ^*, σ (d) π^*, π

12. From which hapticity, dinitrogen binds with metal and is considered to be like that of the iso-electronic CO ligand.

(a) η^5 (b) η^1 (c) η^2 (d) η^4

13. What will be the product of the given reaction

$$[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+} \rightarrow A$$

(a) $A = [N_2Ru(NH_3)_5]^{2+}$ (b) $A = [Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+}$

(c) $A = [Ru(NH_3)_5N_2Ru(NH_3)_5]^{2+}$ (d) $A = [Ru(NH_3)_5N_2]$

14. N_2 has molecular orbitals rather similar to those of CO. Would you expect N_2 to be a stronger or weaker π – acceptor than CO.

(a) Stronger than CO (b) Same as CO

(c) Weaker than CO (d) Can't predict

15. The binding modes of NO in 18 electron compounds $[CoCl(en)_2(NO)]^+$ and $[Co(diars)(NO)]^{2+}$ respectively are:

(a) linear and bent (b) bent and linear (c) linear and linear (d) bent and bent

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ANSWERS

1.	(c)	6.	(c)	11.	(a)
2.	(b)	7.	(b)	12.	(b)
3.	(c)	8.	(b)	13.	(b)
4.	(c)	9.	(c)	14.	(c)
5.	(c)	10.	(b)	15.	(b)

HINT & SOLUTIONS

1. (c)

Sol. NO contains one more electron than CO in N – O π^* orbital and thus act as a three electron donor, i.e. linear NO.

However, NO can also act as one electron donar when the lone pair resides on the nitrogen and the geometry is in the bent form.

2. (b)

Sol.

$$\underset{\substack{5+6-1=10 \\ \text{Linear molecular geometry} \\ N\equiv O}}{NO^+} \xleftrightarrow{\text{isoelectronic}} \underset{\substack{4+6=10 \\ \text{Linear molecular geometry} \\ C\equiv O}}{CO}$$

3. (c)

Sol. Since the complex obeys 18 e^- – rule

$\therefore$ $[Ni(CO)_3(NO)]^x$ has total electron count as –

$10 + 3 \times 2 + 3 + x = 18$

$10 + 6 + 3 + x = 18$

$19 + x = 18$

$x = -1$

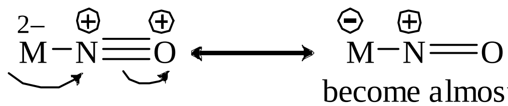
So, the correct answer will be +1 as we know the charge will be of opposite sign to that of calculated by the formula.

4. (c)

Sol. Linear in sp hybridised and bent is sp^2 hybridised

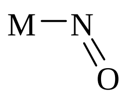
5. (c)

Sol. Linear molecule having sp hybridization



become almost double bond.

Bent having sp^2 hybridization

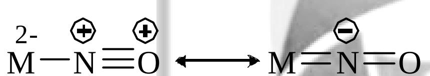


double bond

$\therefore$ option 'c' is the right ans.

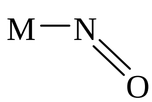
6. (c)

Sol. Linear mode



π bond (M – N bond)

Bent mode



σ – bond

7. (b)

Sol. $Fe(CO)_2(NO)_2 \xleftrightarrow{\text{isoelectronic}} Fe(CO)_5$

$8 + 4 + 6 = 18\ e^-$ $\qquad$ $8 + 10 = 18\ e^-$

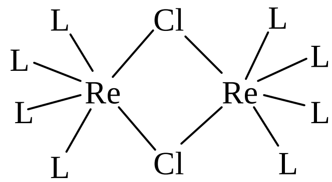
8. (b)

9. (c)

Sol. N_2 is the colourless gas that is liberated.

$\therefore$ The product must be a dimer as it has CN = 5 and it can dimerise to form CN – 6. Since, the new complex obeys the 18 e^- – rule therefore Cl atom must be at bridge

Structural



TEC $= 7 \times 2 + 3 \times 2 + 2 \times 8$

$= 14 + 6 + 16$

$= 36$

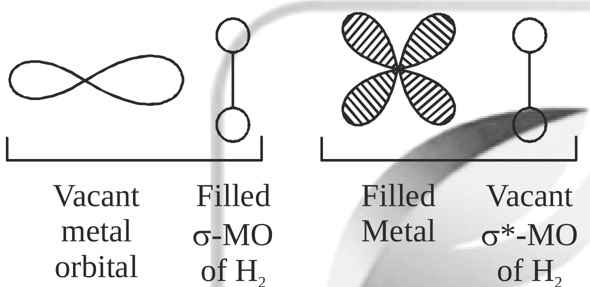
$\therefore$ each Re has 18 e^- and there is no M – M bond present.

10. (b)

Sol. Acidity of M – H bond $\propto$ π – acceptor ability

11. (a)

Sol.



H_2 to M donation **M to H_2 donation**

12. (b)

Sol. Dinitrogen can bind with metal in a number of different ways. The majority of complexes have terminal monohapto link, $\eta^1 - N_2$ in which the bonding can be considered to be like that of isoelectronic CO ligand.

13. (b)

Sol. The unexpectedly strong nucleophilicity of dinitrogen shown by the its displacement of water and is also exhibited in the formation of a bridged complex.

$$[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+}$$
$$\downarrow$$
$$[Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+} + H_2O$$

14. (c)

Sol. The N_2 σ and π levels are very close together in energy and they are all symmetric. The CO levels are farther apart in energy and skewed toward C. Therefore, the geometric overlap for CO is better and CO has better σ-donor and π-acceptor qualities than N_2.

15. (b)

Sol. TEC of $[CoCl(en)_2(NO)]^+$

$\Rightarrow 9 + 1 + 2 \times 4 + x - 1 = 18$

$\Rightarrow x + 17 = 18$

$x = 18 - 17$

$x = 1$

$\therefore$ Bent form

TEC of $[Co(diars)NO]^{+2}$ is

$\Rightarrow 9 + 8 + x - 2 = 18$

$\Rightarrow 15 + x = 18$

$\Rightarrow x = 18 - 15$

$\Rightarrow x = 3$

$\therefore$ Linear form

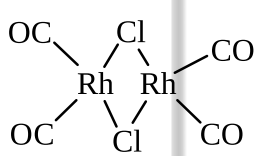
×××××

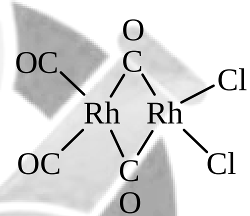
DPP - 07 METAL CARBONYLS

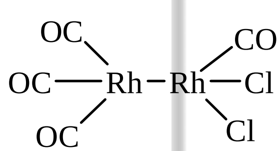
1. In $Mo(CO)_3(PF_3)_3$ & $Mo(CO)_3(PPh_3)_3$ which of the following has highest ν_{CO} order or M – Co back donation:

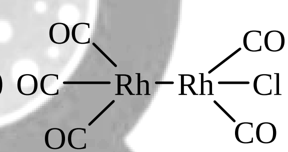
(a) $Mo(CO)_3(PF_3)_3$ (b) $Mo(CO)_3(PPh_3)_3$ (c) both (d) None

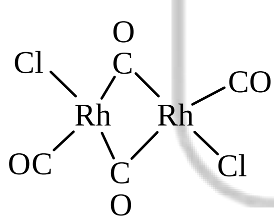
2. The $16e^{\ominus}$ dirhodium complex $Rh_2(CO)_4Cl_2$ have five structural isomers possible, predict the most probable structure among the five structural isomers possible is

(a) 

(b) 

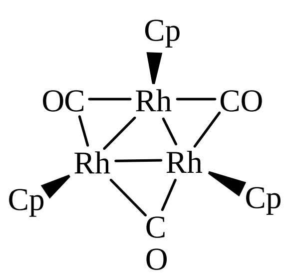
(c) 

(d) 

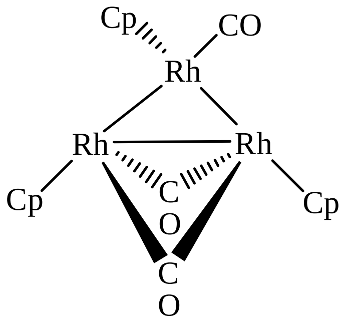
(e) 

3. Match the appropriate set of ν_{CO} stretching infrared spectral bend with trimetallic tricarbonyl complexes:

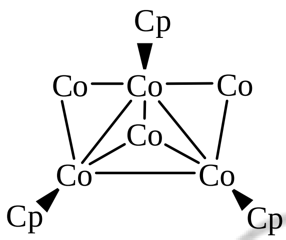
Complexes ν_{C-O}

(1) 

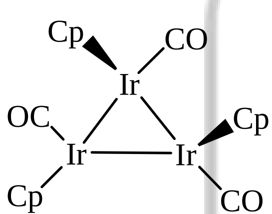
(A) 1833, 1775, 1673 cm^{-1}

(2) 

(B) 1827, 1783, 1766 cm^{-1}

(C) 

(C) 1960, 1918 cm^{-1}

(D) 

(D) 1935, 1975, 1953 cm^{-1}

(E) 1773, 1827, 1794, 1744 cm^{-1}

(a) (i) – A, (ii) – B, (iii) – C, (iv) – D (b) (i) – C, (ii) – A, (iii) – D, (iv) – E
(c) (i) – B, (ii) – A, (iii) – D, (iv) – E (d) (i) – C, (ii) – B, (iii) – A, (iv) – E

4. The V – C bond distances in $V(CO)_6^-$ & V $(CO)_6$ respectively are:
(a) 1.93 & 2.00Å (b) 2.00 & 1.93Å (c) 1.93 & 1.93Å (d) 2.00 & 2.00Å

5. In a carbonyl complex having a linear OC – M – Co group, how ν_{CO} will change when Co is replaced by Et_3N.
(a) Increase (b) decrease (c) remain same (d) disappear

6. Considering NO as a $3e^{\ominus}$ donar, which of the formula of the corresponding natural metal carbonyls which isoelectronic with $Co(NO)_3$ & $Fe(CO)_2(NO)_2$ respectively are:
(a) $Co(NO)_3(CO)$ & $Fe(CO)_5$ (b) $Co(NO)(CO)_3$ & $Fe(CO)_5$
(c) $Co(NO)_6$ & $Fe(CO)_4NO$ (d) $Co(CO)_6$ & $Fe(NO)_4$ CO

7. The no. of isomer formed by CO_2 $(CO)_8$ are:
(a) 2 (b) 3 (c) 4 (d) 5

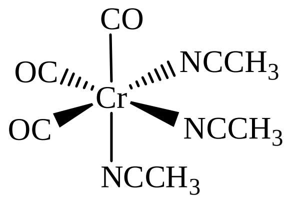
8. The correct stretching frequency order of carbonyl:
(a) semibridging > isocarbonyl > σ/π assymetric bridge
(b) isocarbonyl > semibridging > σ/π assymetric bridge
(c) isocarbonyl > σ/π assymetric bridge > semibridging

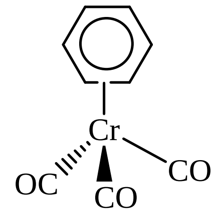
(d) isocarbonyl = σ/π assymetric bridge = semibridging.

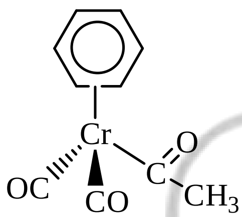
9. Disproportionation of Mn_2 in presence of suitable ligand like Py often leading to formation of:

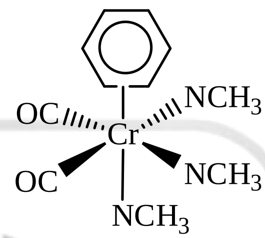
(a) $[Mn(Py)_6]^{2+}$ (b) $[Mn(CO)_5]^{-}$ (c) Both (d) None of these

10. After refluxing of $Cr(CO)_6$ with CH_3CN compound A will formed then after heating compound A at 25°C in the presence of C_6H_6. Compound B will be formed. The compound B is:

(a) 

(b) 

(c) 

(d) 

11. The Collman's reagent is

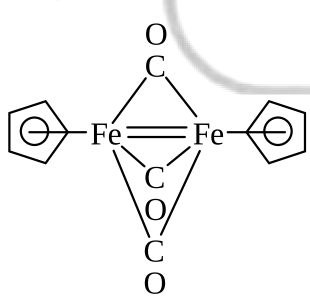
(a) $[Mn(CO)_5]^{-}$ (b) $Na_2Fe(CO)_4$ (c) $V(CO)_6$ (d) $CO_2(CO)_8$

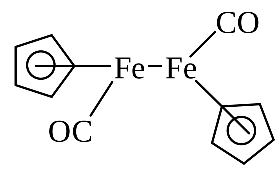
12. The infrared spectrum of $[\eta^5 - CpFe(CO)_2]_2$ when measured at room temperature indicated three bands at 2005, 1961 and 1795 cm^{-1} & when measured at high temperature gave a different spectrum with three bands at 2015, 1973 & 1938 cm^{-1}. Nature of carbonyl group at both room & temperature & high temperature respectively will be:

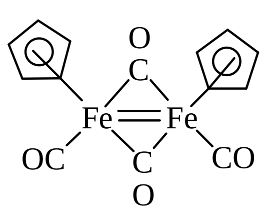
(a) terminal, terminal (b) bridging, terminal

(c) terminal, bridging (d) bridging, bridging

13. Photolysis of $[\eta^5 - CpFe(CO)_2]_2$ at –78°C results in the loss of the colourless, gas & formation of iron containing product having a single carbonyl band at 1785 cm^{-1} & containing 14.7% oxygen by mass, the structure will be.

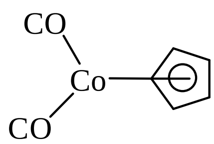
(a) 

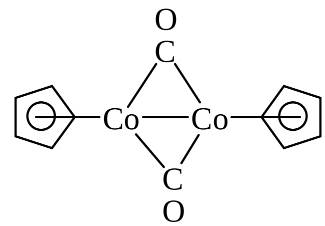
(b) 

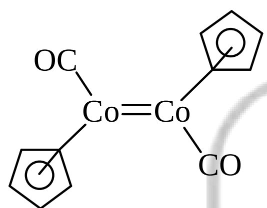
(c) 

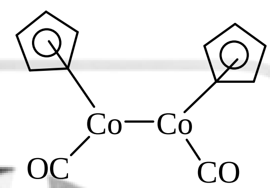
(d) None of these

14. The compound (η^5 - C_5H_5) $Co(CO)_2$ (A) upon UV irradiation, resulted in the evolution of a gas & formation of a new compound B. While the infrared spectrum of A showed absorptions around 1988 cm^{-1}, the spectrum of B shows absorptions only at 1798 cm^{-1}. Compound A & B obey $18e^{\ominus}$ rule and both have cyclopentadienyl group in the η^5-mode the structure of compound B will be:

(a) 

(b) 

(c) 

(d) 

15. Although $17e^{\ominus}$ species $V(CO)_6$ has not found to dimerise to give $V_2(CO)_{12}$, the latter has been found to form along with $V(CO)_6$ & remain stable at extremely low temperatures, then if $V_2(CO)_{12}$ dimer did from than what would be a coordination no.

(a) 5 (b) 6 (c) 7 (d) 8

16. The M – C – M bond angle in bridging carbonyl ligands are—

(a) 120° (b) 90° (c) 112° (d) 130°

17. The number of isomer formed by $CO_2(CO)_8$ in solid and solution state respectively are :

(a) 1, 3 (b) 3, 1 (c) 2, 3 (d) 3, 2

19. (a)

18. In $Os_4(CO)_{14}$ the number of carbonyl ligands in semibridging and nonbridgings respectively are—

(a) 4,1 (b) 4, 10 (c) 40, 4 (d) 1, 4

19. In which carbonyl complex a ≠ b & $\alpha \neq \beta$:

(a) Symmetric μ_2 – CO (b) Semibridging μ_2 – CO

(c) α/π asymmetric bridge(d) isocarbonyl coordination

20. The correct order of cone angle of phosophines are:

(a) $P(CF_3)_3 > P(OPh)_3 > PMe_3 > PF_3$ (b) $PF_3 > PMe_3 > P(OPh)_3 > P(CF_3)_3$

(c) $PMe_3 > P(OPh)_3 > PF_3 > P(CF_3)_3$ (d) $P(OPh)_3 > P(CF_3)_3 > PF_3 > PMe_3$

××××××

QUANTA CHEMISTRY

An Institute of Chemical Sciences

ANSWERS

1. (a)
2. (a)
3. (b)
4. (a)
5. (b)
6. (b)
7. (a)
8. ()
9. (a)
10. (a)
11. (b)
12. (b)
13. (a)
14. (b)
15. (c)
16. (b)
17. (a)
18. (b)
19. (b)
20. (a)

HINT & SOLUTIONS

1. (a)

Sol. π-accepting order of PR_3 is

$PF_3 > P(OPh)_3 > P(OMe)_3 > PPh_3 > PMe_3 \mid P^{+}Bu_3$

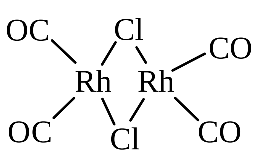
PF_3 is better p-acceptor in comparison to PPh_3 so stretching frequency value

$$Mo(CO)_3(PF_3)_3 \Rightarrow \bar{\nu}_{CO} = 2090 \,\&\, 2055\ cm^{-1}$$

$$Mo(CO)_3(PPh_3)_3 \Rightarrow \bar{\nu}_{CO} = 1937 \,\&\, 1841\ cm^{-1}$$

2. (a)

Sol.



$= 2Rh + 2Cl + 4CO = 18 + 2 \times 3 + 4 \times 2$

$= 18 + 6 + 8 = 32$

per metal = $\frac{32}{2} = 16e^{\ominus}$

3. (b)

Sol.

CO	ν_{CO}
terminal CO	$2130 - 1850\ cm^{-1}$
μ^2 – CO	$1850 - 1750\ cm^{-1}$
μ^3 – CO	$1730 - 1620\ cm^{-1}$

4. (a)

Sol. In $V(CO)_6^-$ negative charge increase metal carbonyl back-π-bonding hence bond length decrease & in $V(CO)_6$ metal carbonyl back-π-bonding also present but in comparison to $V(CO)_6$ is less. So its bond length will increase.

5. (b)

Sol. When Co is replaced by Et_3N then back-π-bonding will increase & ν_{CO} order decrease.

6. (b)

Sol. 2NO = 3CO

(a) $Co(NO)_3 = 9 + 9 = 18e^{\ominus}$

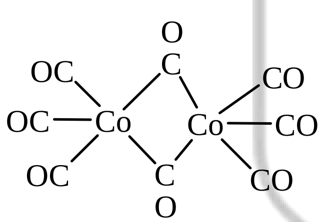
$Co(NO)(CO)_3 = 9 + 3 + 6 = 18e^{\ominus}$

(b) $Fe(Co)_2\ (NO)_2 = 8 + 4 + 6 = 18e^{\ominus}$

$Fe(Co)_5\ = 8 + 10 = 18e^{\ominus}$

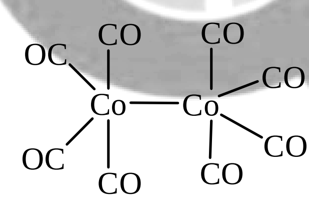
7. (a)

Sol. $CO_2\ (CO)_8$ has 2 isomers one with no bridging carbonyls and another with two bridging carbonyl groups.



(Solid)

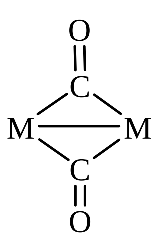
&



(Solution)

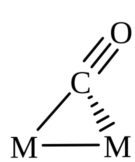
8. ()

Sol.



Semibridging

$\nu_{Co(bt)}$, 1832, 1871 cm^{-1}.



σ/π assymetric bridge

1645 cm^{-1}.

M – C = O – M

isocarbonyl coordination

1835 cm^{-1}.

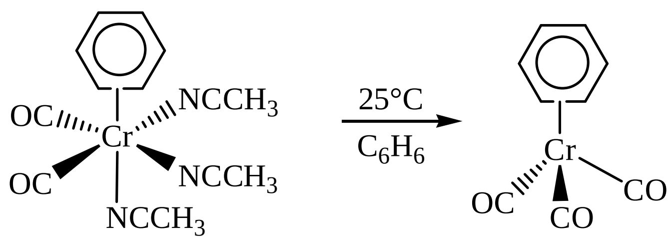
9. (a)

Sol. Disproportionation in the presence of suitable ligands often leading to carbonyl anions

$$3Mn_2(CO)_{10} + 12Py \xrightarrow[-10Co]{120°C} 2[Mn(Py)_6]^{2+} + 4[Mn(CO)_5]^-$$

10. (a)

Sol.



11. (b)

Sol. $Na_2Fe(CO)_4$ called collman's reagent, has found many application in organic synthesis.

12. (b)

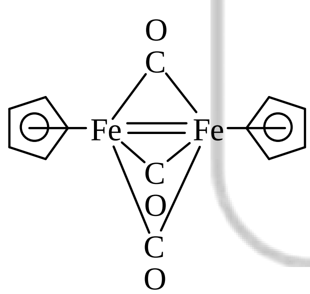
Sol. The room temperature bands of $[\eta^5 - CpFe(CO)_2]_2$ indicates the present of terminal & bridging carbonyl groups & high temperature bands of $[\eta^5 - CpFe(CO)_2]_2$ indicate only terminal carbonyls.

13. (a)

Sol. $[\eta^5 - CpFe(CO)_2]_2 = 17e^{\Theta}$ per metal 1 M – M bond since one Co is lost ($2e^{\Theta}$ are (OSt), therefore one additional bond will form in the molecule.

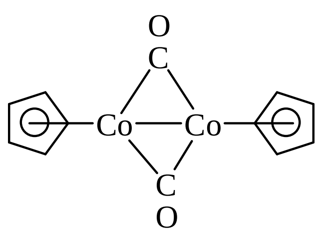
$[\eta^5 - Cp_2Fe_2(CO)_4] \rightarrow \eta^5 - Cp_2Fe_2(CO)_3 + Co$

$16 + 10 + 6 = 32 = 16^{\Theta}$ per metal.



14. (b)

Sol. Infrared absorption of B indicates only bridging carbonyl to attain $18e^{\Theta}$ rule, dimerisation will take place with the formation of a Co – Co double bond.



15. (c)

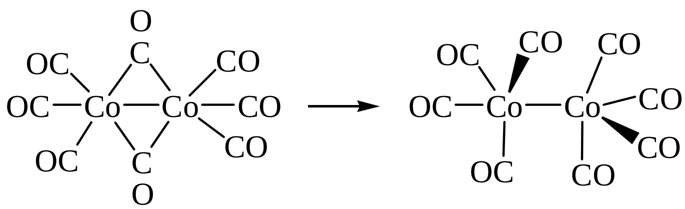
Sol. If the $V_2(CO)_{12}$ dimer did from, it would give each metal a coordination number of 7, which may present too much steric hindrance to allow stability.

16. (b)

Sol. The M – C – M bond angle is 90° or less in bridging carbonyl ligands.

17. (a)

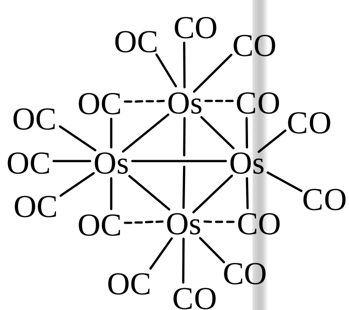
Sol. In solid states $CO_2(CO)_8$ formed one isomer & in solution state it will form 3 isomer.



Solid state Solution state

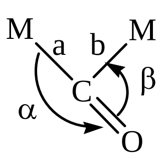
Other two isomer of solution states are uncertain but neither contains bridging carbonyl ligands.

18. (b)

Sol. 

In $Os_4(CO)_{14}$, for of the carbonyl ligands are weakly semibridging and ten are nonbridging.

19. (b)

Sol. 

$\alpha \neq \beta$

$a \neq b$

In semibridging M_2 – CO $\alpha \neq \beta$, $a \neq b$ are found.

20. (a)

Sol. $P(CF_3)_3 > P(OPh)_3 > PMe_3 > PF_3$

137° > 128° > 118° > 104°

××××××

QUANTA CHEMISTRY

An Institute of Chemical Sciences

DPP - 08 METAL CARBONYLS

1. The correct order of Tolman's electronic parameter (χ) of selected phosphine:

(a) $PH_3 > PCl_3 > P(OMe)_3 > P(Oph)_3$ (b) $PCl_3 > P(OPh)_3 > P(OMe)_3 > PH_3$

(c) $PCl_3 > P(OPh)_3 > PH_3 > P(OMe)_3$ (d) $P(OPh)_3 > PCl_3 > P(OMe)_3 > PH_3$

2. The correct order of basicity of phosphines:

(a) $PhPEt_2 > P(Bu^n)_3 > PMe_3 > PEt_3P$ (b) $PEt_3 > PMe_3 > P(Bu^n)_3 > PhPEt_2$

(c) $P(Bu^n)_3 > PhPEt_3 > PEt_3 > PMe_3$ (d) $PMe_3 > PEt_3 > PhPEt_2 > P(Bu^n)_3$

3. Which of the following complex is isostructural with P_4 molecular

(a) $Mn_2(CO)_{10}$ (b) $Os(CO)_4$ (c) $Ir_4(CO)_{12}$ (d) $H_2Fe(CO)_4$

4. Which of the following dihydride was first synthesised which is yellow liquid, unstable above –10°C and behaves as a dibasic acid in water.

(a) $H_2Mn(CO)_5$ (b) $H_2V(CO)_6$ (c) $H_2Fe(CO)_4$ (d) $H_2Co(CO)_4$

5. Complexes which contain the $\eta_2 - H_2$ ligand are now referred as—

(a) classical (b) nonclassical (c) both (d) None

6. The reaction of $CO_2(CO)_8$ with sodium amalgam followed by methyl iodide leads to formation of

(a) $Me_3(CO)_3Co$ (b) $(Me(O)_3Co(CO)_3$ (c) $MeCo(CO)_4$ (d) $MeCo(CO)_4I$

7. When $RhCl_3.3H_2O$ reach with Co in presence of MeOH at 100°C & 1 atm pressure. Complex (A) will be formed, when this complex A react with heptane in presence of CO, H_2O & $NaHCO_3$. Compound (B) will form compounds (A) & (B) respectively are.

(a) $[Rh(CO)_2]_2Cl$, $Rh(CO)_5$ (b) $[Rh(CO)_2Cl]_2$, $Rh_4(CO)_{12}$

(c) $[Rh(CO)_2Cl]_2$, $Rh(CO)_5$ (d) $[Rh(CO)_2]_2Cl_2$, $Rh_4(CO)_{12}$

8. Treatment of $TiCl_4$ at low temperature with EtMgBr gives an organometallic compound (A) that is unstable above –70°C, however, treatment of $TiCl_4$ at low temperature with MeLi or $LiCH_2SiMe_3$, give stable compound (B) this is due to.

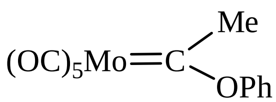
(a) The compound (A) is formed by the action of grignard reagent & the said reagent is unstable at high temperature.

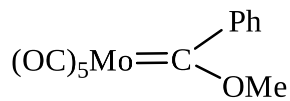
(b) The compound (B) is formed by the action of organolithium reagent & the said reagent is stable even at high temperature.

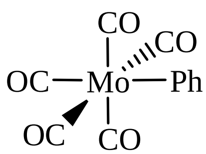
(c) The compound (A) undergoes α-elimination therefore the said compound is unstable an high temperature.

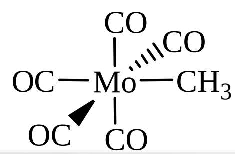
(d) The compound (A) undergoes β-elimination at high temperature whereas, in compound (B) there is no chance for π-elimination even at low & high temperature.

9. When $[Mo(CO)_6]$ is allowed to react first with LiPh & with the strong carbocation reagent $CH_3OSO_2CF_3$ to give a product ‘A’. The structure A will be

(a) 

(b) 

(c) 

(d) 

10. $[Cr(CO)_6]$ react with excess of NO, formed compound will be

(a) $[Cr(CO)_5(NO)]$ (b) $[Cr(CO)_4(NO)]$ (c) $Cr(CO)_4(NO)_2]$ (d) $[Cr(NO)_4]$

11. The increasing order of acidity of the following phosphines are:

(a) $HCo(CO)_3(PF_3) > HCo(CO)_3(PMe_3) > HCo(CO)_3(PPh_3)$

(b) $HCo(CO)_3(PMe_3) > HCo(CO)_3(PPh_3) > HCo(CO)_3(PF_3)$

(c) $HCo(CO)_3(PF_3) > HCo(CO)_3(PPh_3) > HCo(CO)_3(PMe_3)$

(d) $HCo(CO)_3(PPh_3) > HCo(CO)_3(PF_3) > HCo(CO)_3(PMe_3)$

12. The final producrt in the reaction:

$[Mn(CO)_6]^+ + MeLi \rightarrow$ is:

(a) $[Mn(CO)_6]^-Me$ (b) $[Mn(CO)_5]Me]$ (c) $[Mn(CO)_6]$ (d) $[(Me(O)\ Mn(CO)_5]$

13. Which of the following complex contain both bent & linear nitrosyl groups are:

(a) $[Ir(PPh_3)_2(CO)(NO)Cl]^+$ (b) $[Ru(PPh_3)_2(NO)_2Cl]^+$

(c) $[C\eta^5 - C_5H_5)\ Re(CO)_2NO]^+$ (d) $Fe(CO)_2(NO)_2$

14. $[Mn(CO)_6]^+ \xrightarrow[2.\Delta]{1.H_2O} P$

(a) $[Mn(CO)_6(H_2O]$ (b) $[(CO)_5Mn(COOH)]$ (c) $[Mn(CO)_6H]^+$ (d) $[HMn(C)_5]$

15. When $Co_2(CO)_8$ react with $CHCl_3$ yields compound (A) with molecular formula $Co_3CH(O)_9$. Both IR and NMR data indicate the presence of only terminal CO ligand & the structure is symmetrical on the above information which of the following statement about the structure (A) is not correct.

(a) The compound (A) follow $18e^{\ominus}$ rule.

(b) the number of per M – M total no. of M – M bonds are 3 and 2 respectively.

(c) the oxidation state of the metal Co in product (A) is +1.

(d) it has a carbido ligand which present in μ^3 bonding mode.

16. In the reaction given below—

$[Ir(CO)(Cl)(PPh_3)_2] \xrightarrow[D]{PEt_3} P$

The major product 'P' & their respective mechanism for the formation of product as:

(a) $[Ir(CO)(Cl)(PPh_3)(PEt_3) + PPh_3$, dissociative

(b) $[Ir(CO)(Cl)(PPh_3)(PEt_3)(PEt_3)] + PPh_3$, associative

(c) $[Ir(PPh_3)(Cl)(PEt_3) + CO$, associative

(d) $[Ir(PPh_3)(Cl)(PEt_3) + CO$, dissociative

17. $[\eta^5$ - $CpFe(CO)_4$ (A) is a dark green solid compound. The IR spectrum shows a single CO stretching band at 1640 m^{-1}. The ^{1}HNMR spectrum shows a single line even at low temperature, which of the following statement is not true on the basis of given data about the structure of $[\eta^5$ - $CpFe(CO)_4$

(a) The complex (A) follows the 18 electron rule.

(b) The total number of M – M bonds in the complex are six.

(c) All CO's are present μ^3-mode

(d) The CO's are present in μ^2-mode where as another two CO's are present at μ^3-modes.

18. Consider the compound $[C_8H_8)$ $Ru(CO)_3$, which is likely to be the best description of the C_8H_8 ligand.

(a) it is bonded in an η^8-manner to the Ru atom and one ^{1}H NMR signal is observed over a range of temperature.

(b) it is a bonded in an η^4-manner to the Ru atom, but ^{1}H NMR signal is observed in the limiting high temperature spectrum.

(c) it is a bonded in an η^3-manner to the Ru atom and the ^{1}H NMR spectrum is consistent with a stereochemically non-rigid molecule.

(d) it is a bonded in an η^3-manner to the Ru atom and ^{1}H NMR spectrum is consistent with a static structure.

19. The reaction of $(\eta^6 - C_7H_8)$ $Mo(CO)_3$ with $[Ph_3C]$ $[BF_4]$ results in :

(a) proton abstraction & formation of $[(\eta^7 - C_7H_8)$ $Mo(CO)_3]^-$

(b) proton abstraction & formation of $[(\eta^5 - C_7H_7)$ $Mo(CO)_3]^-$

(c) proton abstraction & formation of $[(\eta^5 - C_7H_8)$ $Mo(CO)_3]^+$

(d) proton abstraction & formation of $[(\eta^5 - C_7H_8)$ $Mo(CO)_3]^+$

20. Which statement is incorrect about CO ligands?

(a) A CO ligands can accept electrons into its π*MO; this weakness the C – O bond.

(b) In the IR spectrum of $Fe(CO)_5$, absorption assigned the CO stretching modes are at higher wave number than that of free CO.

(c) CO ligands can adopt terminal, μ and μ_3 bonding modes, the amount of back donation depends on the bonding mode.

(d) fluxional behaviour is common in metal carbonyl compounds, and can be investigated by ^{13}C NMR spectroscopy.

××××

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ANSWERS

1. (c)
2. (b)
3. (c)
4. (c)
5. (b)
6. (c)
7. (b)
8. (d)
9. (b)
10. (d)
11. (c)
12. (d)
13. (b)
14. (d)
15. (b)
16. (b)
17. (d)
18. (b)
19. (d)
20. (b)

HINT & SOLUTIONS

1. (c)

Sol. $PCl_3 > P(OPh)_3 > PH_3 > P(OMe)_3$

40.9 29.2 27.1 23.4

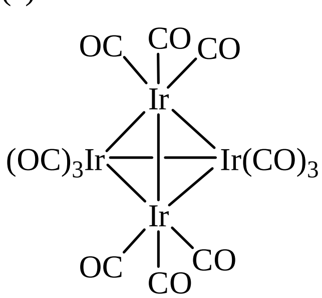
2. (b)

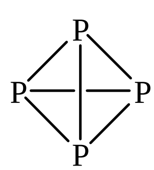
Sol. $PEt_3 > PMe_3 > P(Bu^n)_3 > PhPEt_2$

8.69 8.65 8.43 6.25

3. (c)

Sol.

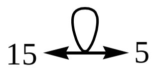




both are tetramers.

$[Ir(CO)_3]_4 = 9 + 6 = 15$

$P_4 = 5$



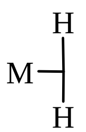
4. (c)

Sol. $H_2Fe(CO)_4 = 18e^{\ominus}$

it is the dihydride which synthesized first.

5. (b)

Sol.



Nonclassical

Complex which contain the $\eta_2 - H_2$ ligand are none refered to as nonclassical.

6. (c)

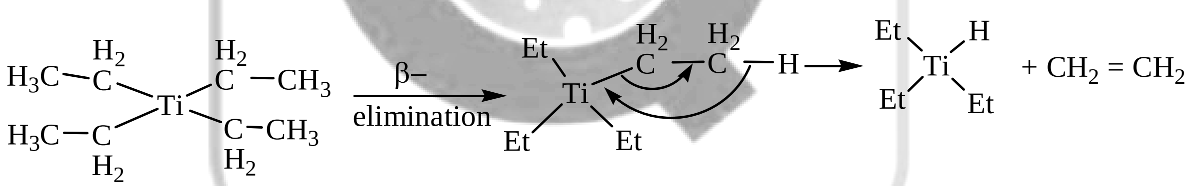
Sol. $CO_2(CO)_8 + 2Na \rightarrow 2Na(Co(CO)_4] \rightarrow [Co(CO)_4]^- \xrightarrow{Me-I} [MeCo(CO)_4]$

7. (b)

Sol. $RhCl_3.3H_2O + CO \xrightarrow[100°C,\ 1\ atm]{MeOH} [Rh(CO)_2Cl]_2 \xrightarrow[CO,\ H_2O,\ NaHCO_3]{heptane} Rh_3(CO)_{12}$

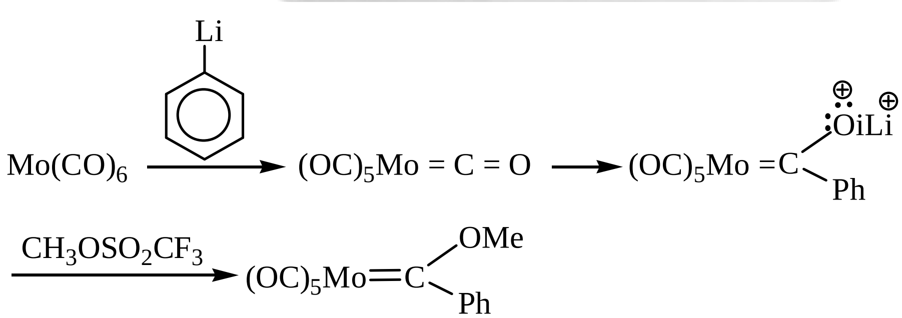
8. (d)

Sol.



9. (b)

Sol.



10. (d)

Sol. $[CrCO)_6] = 6 + 6 \times 2 = 6 + 12 = 18e^{\ominus}$

4 NO = 6 CO.

$[Cr(NO)_4] = 6 + 4 \times 3 = 6 + 12 = 18e^{\ominus}$

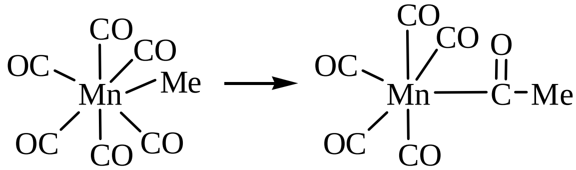
11. (c)

Sol. $HCo(CO)_3(PF_3) > HCo(CO)_3(PPh_3) > HCo(CO)_3(PMe_3)$

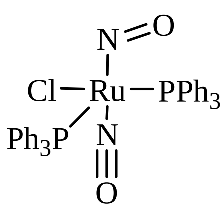
The acidic character of metal carbonyl hydrides decreases on descending the group in periodic table & more will be the π-acceptor ligand present on phosphine more will be acidic strength.

12. (d)

Sol. $[Mn(CO)_6]^+ + MeLi \xrightarrow{-CO} [Mn(CO)_6]^+ \xrightarrow{\overset{\ominus}{Me}\overset{\oplus}{Li}} [Mn(CO)_6Me] \longrightarrow$

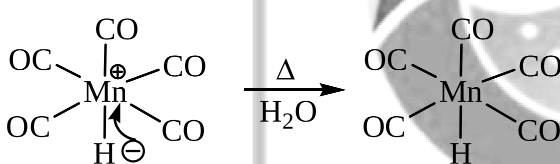


13. (b)

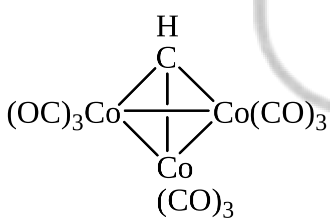
Sol.  $= 8 + 4 + 1 + 3 + 1 - 1 = 18^{\ominus}$

14. (d)

Sol. $[Mn(CO)_6]^+ \xrightarrow[2.\Delta]{1.H_2O} [Mn(CO)_5]^+ 18e^{\ominus}$ dissociative mechanism



15. (b)

Sol.  'CH' contribute '3e' which is μ^3-bridging.

TEC on each Co will be $= 9 + 3 \times 2 + 1 + 1 + 1 = 9 + 6 + 3 = 18e^{\ominus}$

TEC = $Co_3(CH)(CO)_9$ C = M + L

$= 9 \times 3 + 3 \;\; 9 \times 2$ O = Co – 1

$= 48e^{\ominus}$ Co = +1

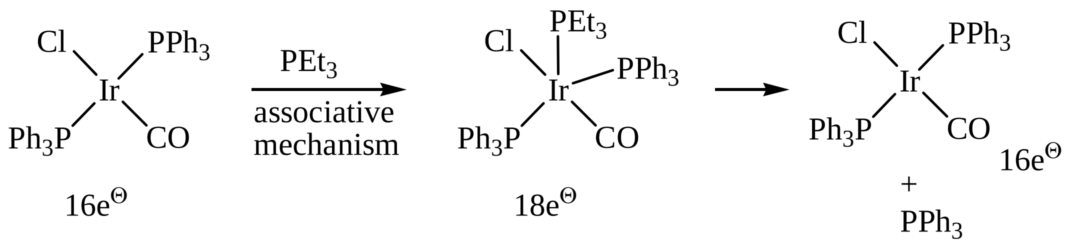
$$M - M \text{ bond} = \frac{18 \times 3 - 48}{2} = \frac{54 - 48}{2} = \frac{6}{2} = 3$$

$$\text{per } M - M \text{ bond} = \frac{48}{3} = 16 = 2M - M$$

The incorrect statement is (b).

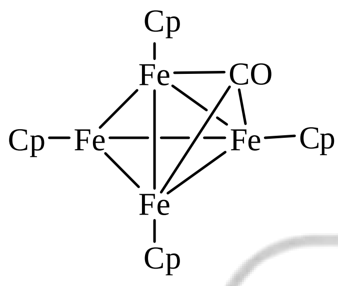
16. (b)

Sol.



17. (d)

Sol.



$[\eta^5\text{ - CpFe(CO)}_4] \rightarrow \text{TVE} = 5 \times 4 + 8 \times 4 + 4 \times 2 = 20 + 32 + 8 = 60$

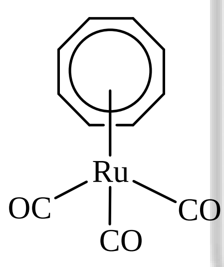
$$\text{M} - \text{M bond} = \frac{n \times 18 - \text{TVE}}{2} = \frac{4 \times 18 - 60}{2} = \frac{12}{2} = 6\text{M} - \text{M}$$

electron per metal = 15 this means each metal makes 3 M – M bond.

$\nu_{CO} = 1640\ cm^{-1}$ indicates μ^3 – CO.

18. (b)

Sol.

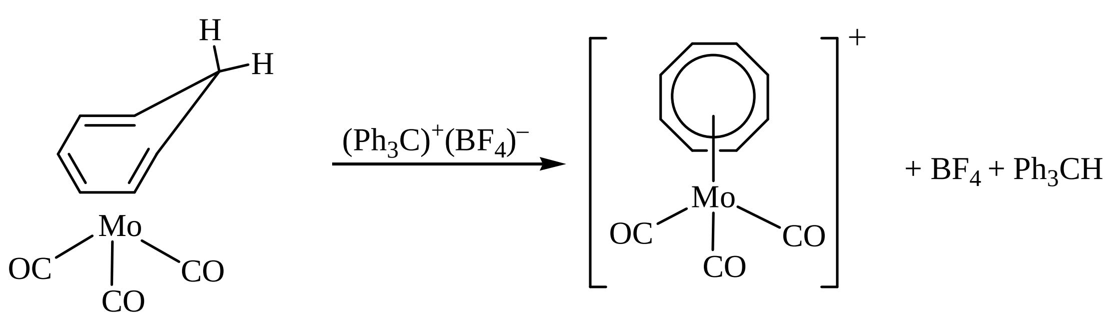


$(C_8H_8)\ Ru(CO)_3 = \eta + 8 + 6 = 18 = \eta + 14 = 18 = \eta = 18 - 14 = 4$

here all hydrogen atom gives 1 signal in ^1H NMR.

19. (d)

Sol. Cycloheptatriene complex can be oxidized (hydride ion abstraction) to form cycloheptatrienyl (some times called tropylium) complexes:



20. (b)

Sol. In the $Fe(CO)_5$ absorption assigned the CO stretching mode are at lower wave number than that of free CO.

×××××

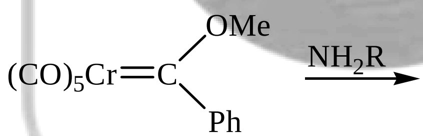
DPP- 09 OMC

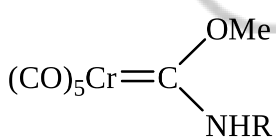
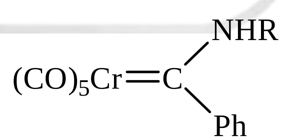
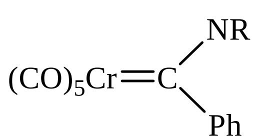
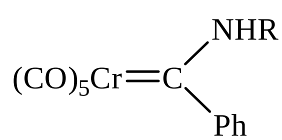
1. The bond order between metal and carbon in fischer carbene is
(a) One (b) Two (c) Less than two (d) Between one and two

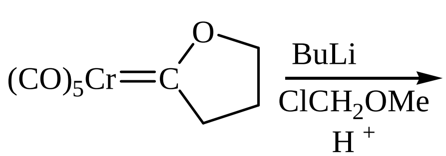
2. Which of the following option does not match with fischer carbene.
(a) Singlet
(b) Electrophilic nature of carbene carbon
(c) Low oxidation state
(d) Nucleophilic nature of carbene carbon

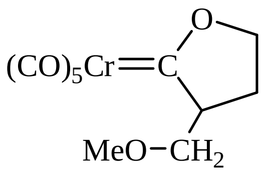
3. Oxidation state of the metal in carbene $(CO)_4(Cl)(NH_2)$ Mo = $CHCH_3$
(a) 2 (b) 3 (c) 1 (d) 4

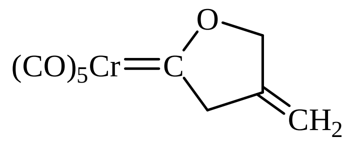
4. Correct match of schrock carbene is
(a) Triplet, electrophilic, bond order = 2
(b) Triplet, nucleophilic, bond order = 2
(c) Triplet, nucleophilic, bond order < 2
(d) Singlet, electrophilic, bond order = 2

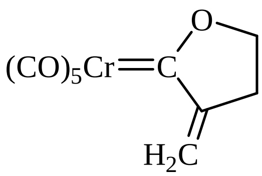
5. The product of 

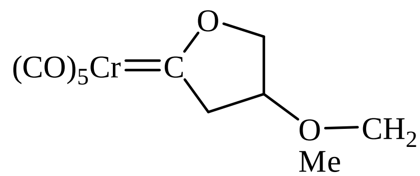
(a) 
(b) 
(c) 
(d) 

6. The product of 

(a) 

(b) 

(c) 

(d) 

7. For $(PPh_3)_5Cr = CHCH_3$ correct statement is

(a) Oxidation state of Cr is +2 and obey $16e^-$ rule.

(b) Oxidation state of Cr is +2 and obey $18e^-$ rule.

(c) Oxidation state of Cr is +3 and obey $18e^-$ rule.

(d) Oxidation state of Cr is +3 and obey $16e^-$ rule.

8. The bond order between double bonded carbon and its substituent except H is lowest in

(a) $(CO)_5\ Mo = CHOCH_3$ (b) $(CO)_5\ Mo = CHNH_2$

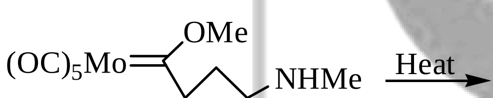
(a) $(CO)_5\ Mo = CHSH$ (d) $(CO)_5\ Mo = CHN(CH_3)_2$

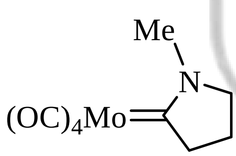
9. The bond order between double bonded carbon and its substituent except H is lowest in

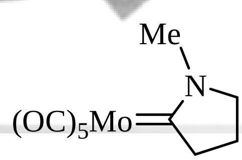
(a) $(CO)_5\ Mo = CHOCH_3$ (b) $(CO)_4\ (NO)\ Mo = CHCH_3$

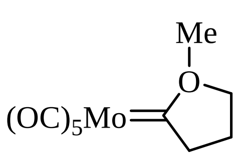
(a) $(CO)_4\ (NH_3)\ Mo = CHCH_3$ (d) $(CO)_4\ (Py)\ Mo = CHCH_3$

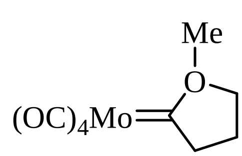
10. Predict the possible product from the proposed reaction.



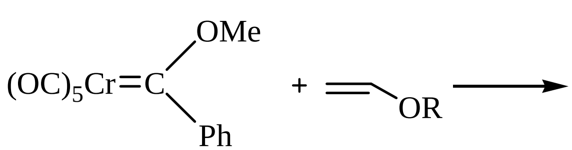
(a) 

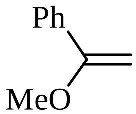
(b) 

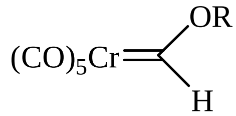
(a) 

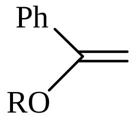
(d) 

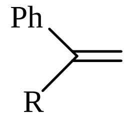
11. The product of the reaction is—



(a) 

(b) 

(c) 

(d) 

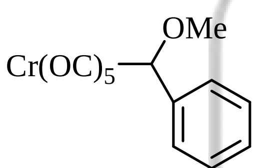
12. Singlet carbene is treated as which of the following and what will be the change in O.S.

(a) Neutral, no change
(b) Neutral, change by 1 unit
(c) dianionic, no change
(d) dicationic, change by 1 unit

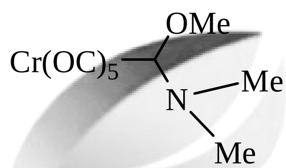
14. The ^{13}C NMR resonance position of the carbene for terminal and bridging group respectively is

(a) 250 – 500 δ and 100 – 210 δ
(b) 100 – 210 δ and 250 – 500 δ
(c) 250 – 500 δ and 0 – 10 δ
(d) 0 – 10 δ and 100 – 210 δ

15. Consider the following structures and predict about Cr – C bond length.



I



II

(a) I > II
(b) II > I
(c) I = II
(d) None of these

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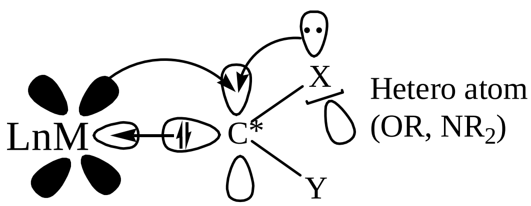
ANSWERS

1. (d)
2. (d)
3. (a)
4. (b)
5. (b)
6. (c)
7. (b)
8. (a)
9. (d)
10. (b)
11. (a)
12. (a)
13. (b)
14. (a)
15. (b)

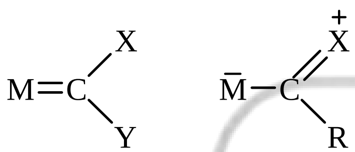
HINT & SOLUTIONS

1. (d)

Sol.



Singlet carbene



Due to the overlapping of hetero atom the bond order in Fishcher carbene of metal and carbene is between one and two.

2. (d)

Sol. In Fischer carbene, metal is in low oxidation state.

$\rightarrow$ Carbenic carbon is electrophilic in nature.

$\rightarrow$ The organic carbene used is singlet carbene.

3. (a)

Sol. OS of Mo is $(CO)_4$ (cl) (NH_2) Mo = $CHCH_3$

$-1 + (-1) + x = 0$

$-2 + x = 0$

$x = 2$

4. (b)

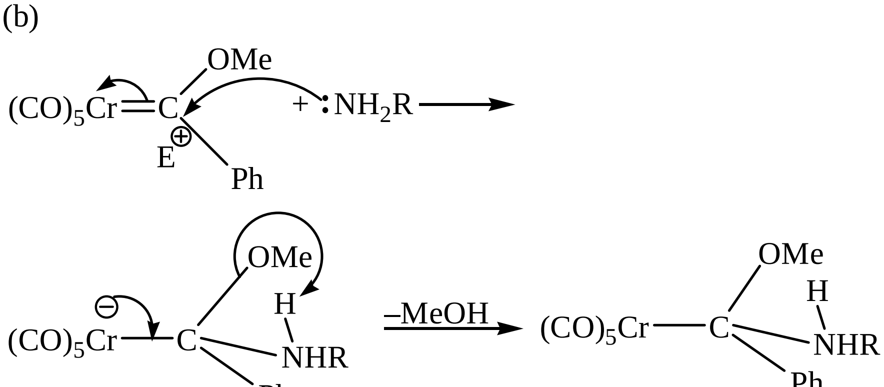
Sol. In schrock carbene, organic carbene used is triplet carbene.

$\rightarrow$ The carbenic carbon is nucleophilic in nature.

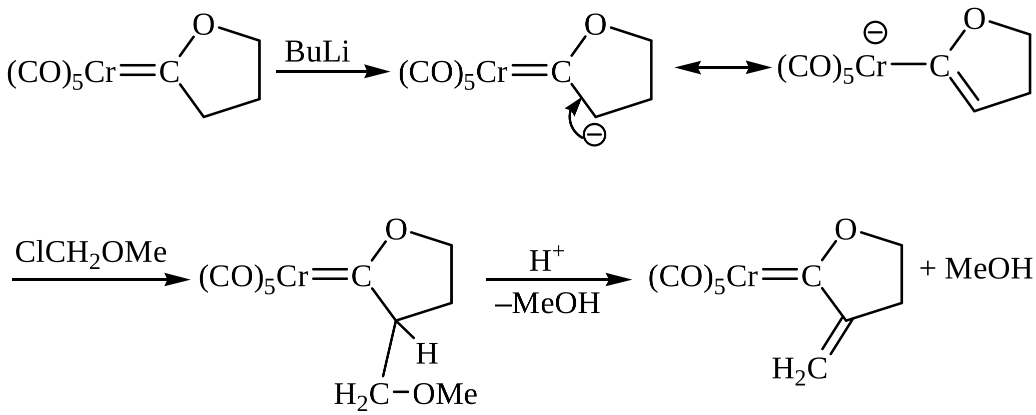
$\rightarrow$ Bond order = 2

5. (b)

Sol.



6. (c)

Sol. 

7. (b)

Sol. O.S. of Cr in $(PPh_3)_5Cr = CHCH_3$ is + 2 and TEC = 5 × 2 + 6 + 2 = 10 + 6 + 2 = 18e$^-$

8. (a)

Sol. Bond order between double bonded carbon and its substituent depends upon electrod-negativity of the substituent.

Extent of back donation $\propto$ Bond order of C – M $\propto$ Electronegativity $\propto \dfrac{1}{\text{B.O. of C – X}}$

$\therefore$ Electronegativity order is

O > N > S.

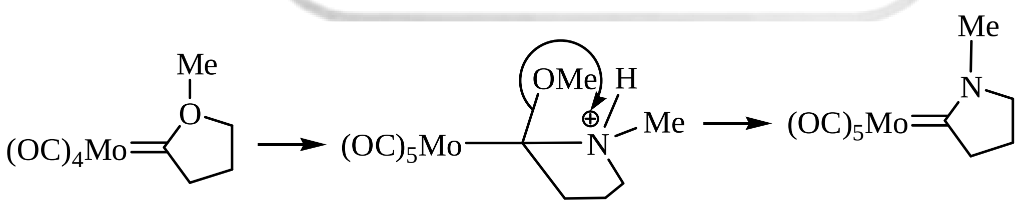
Hence, option 'a' is the right answer.

9. (d)

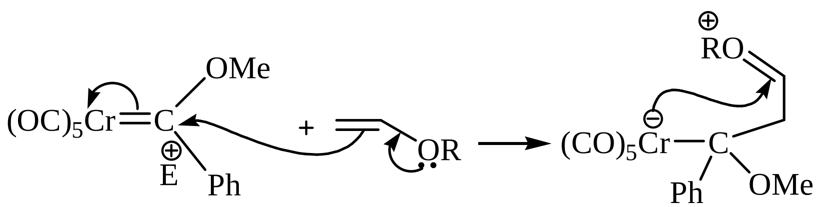
Sol. Metal carbon IR stretching frequency depends upon the ligands present in the complex.

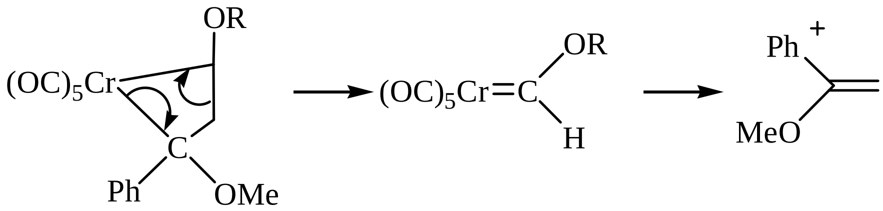
$$\pi - \text{acceptor ligands} \propto \frac{1}{\text{M} - \text{C stretching frequency}}$$

10. (b)

Sol. 

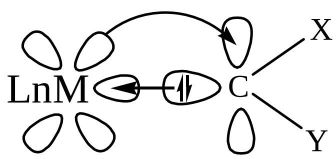
11. (a)

Sol. 



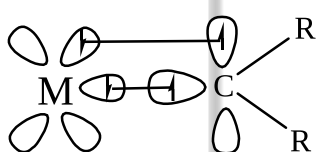
12. (a)

Sol. Singlet carbene is treated as neutral and there is no change in O.S. of carbene metal.



$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} C$$

13. (b)



Sol. dionionic

$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} C$$

14. (a)

Sol. For terminal $\rightarrow$ 250 - 500 δ

For bridging groups $\rightarrow$ 100 – 210 δ with M – M bond

For bridging groups $\rightarrow$ 0 – 10 δ without M – M bond

15. (b)

Sol. The Cr – C bond length is longer is II as compared to I as the carbene carbon is electron deficient in both the cases. However, in I there is only one hetero atom containing electron donating group while in II there are two heteroatom based electron donating groups on the carbene carbon. The effect of the phenyl group seems to be less when compared to the heteroatoms.

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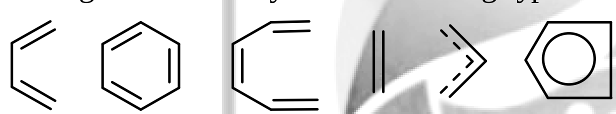
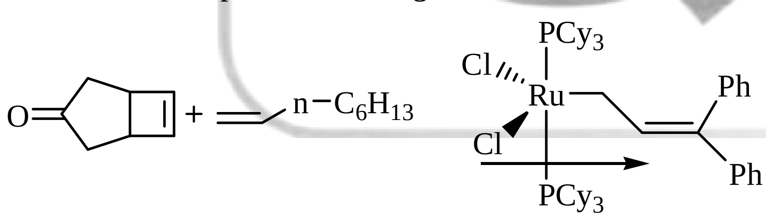
DPP- 10 OMC

1. Which molecular orbital act as electron donor and electron acceptor in C = C respectively.
   (a) σ and π (b) π and $\pi*$ (c) $\pi*$ and π (d) σ and $\pi*$
2. Through which hapticity fullerene attached with metal.
   (a) η^4 (b) η^6 (c) η^2 (d) η^1
3. How many alkene signals are observed in
   $(\eta^5 - Cp)\ Rh\ (\eta^5 - C_2H_4)_2$ at 233 K and 373K respectively.
   (a) 2 and 1 (b) 1 and 2 (c) 2 and 3 (d) 4 and 1
4. Arrange the reactivity of the following types of alkene given

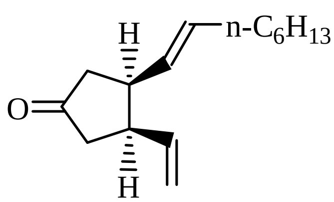


(i) (ii) (iii) (iv) (v) (vi)

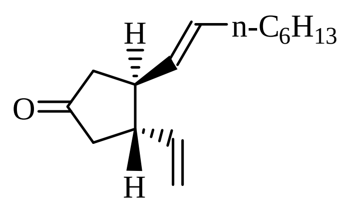
   (a) (i) > (iv) > (ii) > (iii) > (iv) > (vi) (b) (iv) > (i) > (iii) > (iii) > (iv) > (vi)
   (c) (vi) > (v) > (iii) > (i) > (ii) > (iv) (d) (iv) > (vi) > (i) > (iii) > (ii) > (v)
5. What will be the product of the given alkene metathesis reaction.



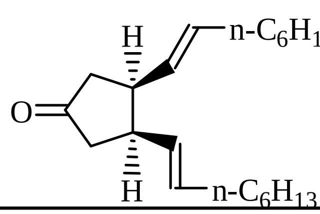
(a)



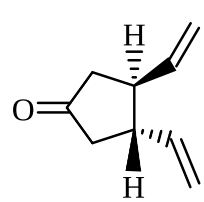
(b)



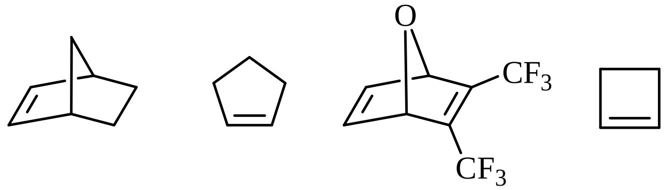
(c)



(d)



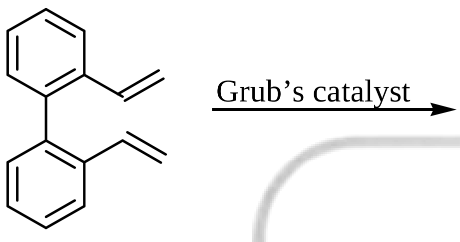
6. Reactivity order of olefins for metathesis

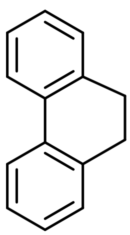
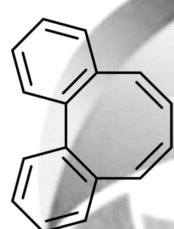
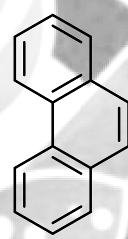
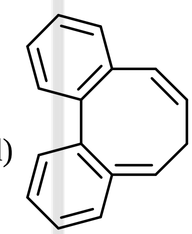


(i) (ii) (iii) (iv)

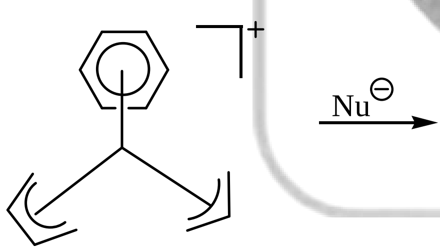
(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (iii) > (ii) > (i)
(c) (iv) > (ii) > (i) > (iii)
(d) (iii) > (i) > (ii) > (iv)

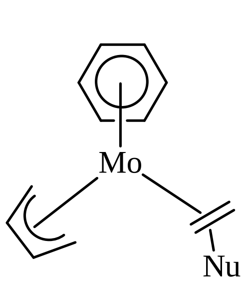
7. What will be the product for the given metathesis reaction.

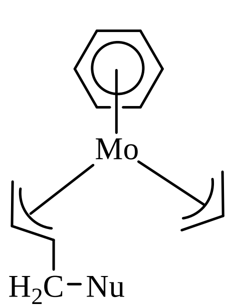


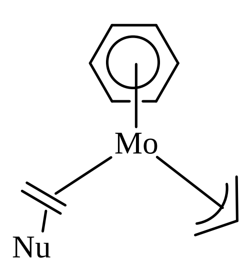
(a) 
(b) 
(c) 
(d) 

8. Product for the given reaction is



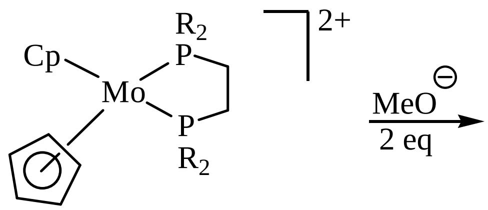
(a) 

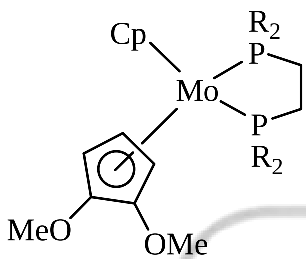
(b) 

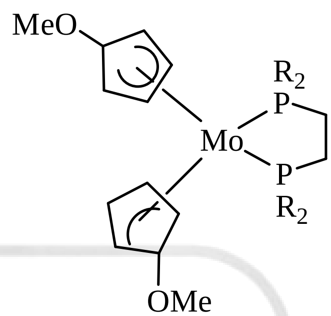
(c) 

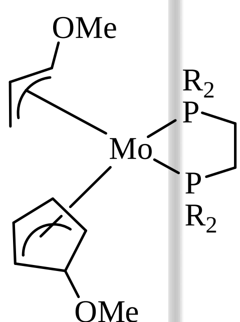
(d) No reaction

9. Predict for the given reaction is



(a) 

(b) 

(c) 

(d) No reaction

10. In metal-olefin interaction, the extent of increase in metal $\rightarrow$ olefin back π-bonding would

(a) Lead to decrease in C = C bond length.

(b) Change the formal oxidation state of the metal.

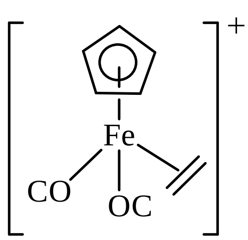
(c) Change the hybridisation of the olefin carbon from sp^2 to sp^3.

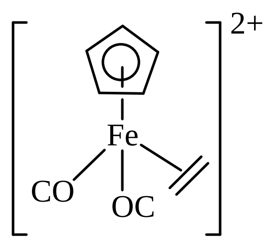
(d) Increase with the presence of electron donating substituents on the olefin.

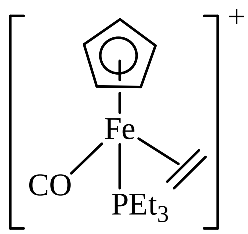
11. Which is not a π-bonded complex.

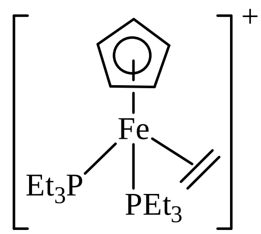
(a) Zeise's salt (b) Ferrocene (c) Dibenzene chromium (d) Tetraethyl lead

12. Arrange the following compounds in the increasing order of ethylene C – C bond length.

(i) 

(ii) 

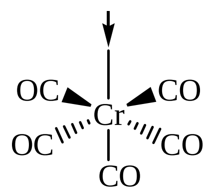
(iii) 

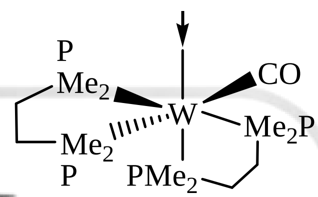
(iv) 

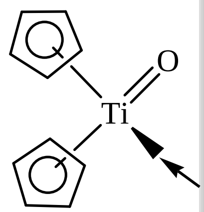
(a) (ii) < (i) < (iii) < (iv) (b) (iv) < (iii) < (ii) < (i)

(c) (ii) < (iiii) < (i) < (iv) (d) (iv) < (ii) < (i) < (iii)

13. To which of the following structures will trifluoroethylene ($F_2C = CHF$) bind most and least strongly respectively.

(i) 

(ii) 

(iii) 

(a) (i) and (ii) (b) (ii) and (iii) (c) (iii) and (i) (d) (ii) and (i)

14. The reactivity order of trans and cis-cyclooctene towards transition metal say Cr.

(a) Trans > cis (b) cis > trans (c) Trans = cis (d) Can‘t determine

15. For metal olefin complexes (i) $[PtCl_3(C_2H_4]^-$ and (ii) $[PtCl_3(C_2F_4)]^-$, the correct statement is

(a) C – C bond length is same both in (i) and (ii)

(b) C – C bond length in (i) is smaller

(c) C – C bond length in (ii) is smaller

(d) A metallacycle is formed in each complex

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QUANTA CHEMISTRY

An Institute of Chemical Sciences

ANSWERS

1. (b)	6. (c)	11. (d)
2. (c)	7. (c)	12. (a)
3. (a)	8. (b)	13. (b)
4. (b)	9. (a)	14. (a)
5. (a)	10. (c)	15. (b)

HINT & SOLUTIONS

1. (b)

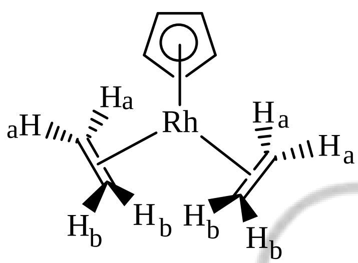
Sol. The C = C π-bonding Mo acts as an electron donor, while the π – MO is an electron acceptor.

2. (c)

Sol. Fullerene attached with metal through η^2 mode.

Eg. Mo $(\eta^4 - C_{60})(CO)_5$

3. (a)

Sol. 

At low temperature i.e. 233K two signals of alkene proton are observed.

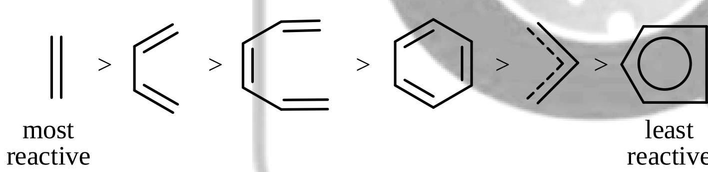
$4H_a \rightarrow$ 1 signal

$4H_b \rightarrow$ 1 signal

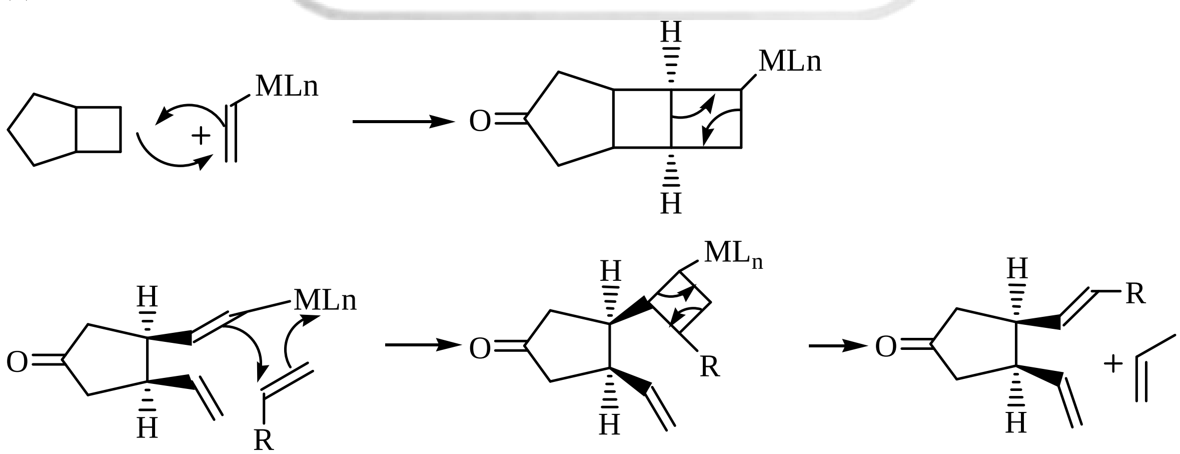
But at high temperature i.e. 373K, the proton environment become equivalent as each alkene ligand rotates about the metal ligand co-ordinate bond. Therefore only 1 signal is observed.

8H _______ 1 signal.

4. (b)

Sol. 

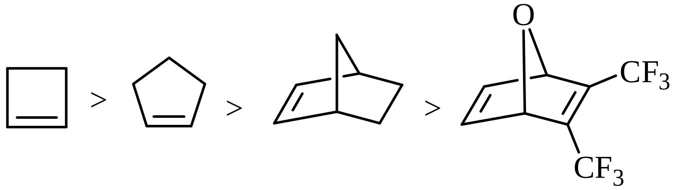
5. (a)



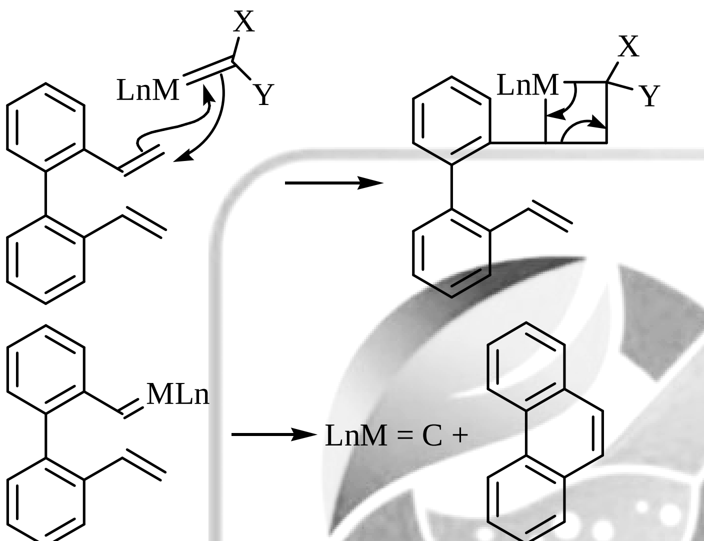
(R = nC_6H_{13})

6. (c)

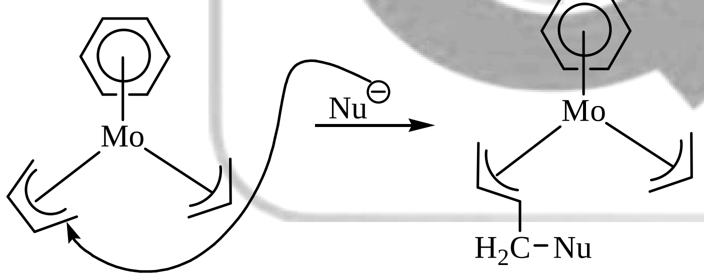
Sol. Olefins such as a cyclohexenes have little or no ring strain and cannot be easily polymerised with the usual catalysts. Strained cyclic olefins such as shown above, have sufficient ring strain to make this process possible.



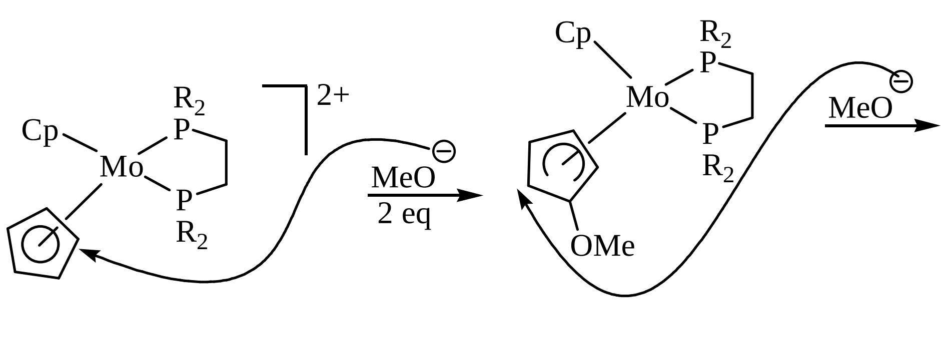
7. (c)

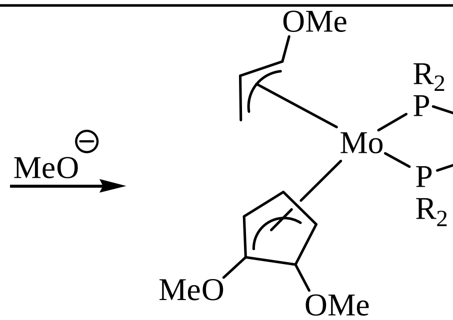
Sol.


8. (b)

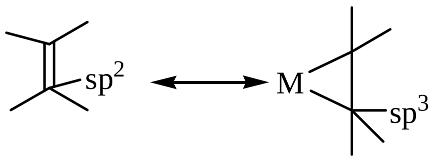
Sol.


9. (a)

Sol.


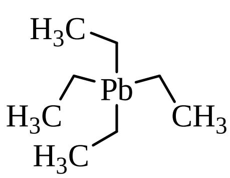


10. (c)

Sol. 

11. (d)

Sol. Tetraethyl lead i.e. $Pb(C_8H_{20})$ is not π-bonded complex. It is σ-bonded organometallic compound.



12. (a)

Sol. In this series, (i) has the shortest C – C bond length, the back donation from Fe to ethylene is lest because of higher positive charge on the complex and the presence of two good π-acceptor CO groups.

and (iv) has the longest C – C bond length indicating the highest back donation to ethylene due to the presence of two good σ-donor Et_3P groups.

13. (b)

Sol. The tungsten complex will bind most strongly since the third row transition metals binds the strongest and also due to the presence of two highly donating biphosphines. Ti^{4+} has no electron density for back donation since it is a d° system.

14. (a)

Sol. Trans cyclo-octene has more strain when compared to the cis-isomer and hence will bind strongly to metal to release this strain.

15. (b)

Sol. As we know in the presence of EWG π-back donation increases due to which M – M bond becomes strong and C – C bond becomes weak.

Since in C_2F_4, F act as EWG hence have C – C bond weak and C – C bond length high.

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QUANTA CHEMISTRY

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DPP- 11 OMC

1. The difference between the Fischer & Schrock carbene is that:

(a) Fischer carbenes are electron rich & can be attacked by electrophiles; schrock carbenes are electron poor & can be attacked by nucleophiles.

(b) Fischer-carbenes are electron poor & can be attacked by nucleophiles; Schrock carbenes are electron rich & can be attacked by electrophiles.

(c) they differ based on the metal they are bonded with it.

(d) None of these

2. Which of the following statement is not true regarding the carbene.

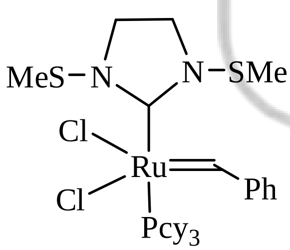
(a) Schrock carbene behave like a phosphorus ylide in some of its reactions.

(b) The carbene carbon of schrock carbene is nucleophilic in nature where as metal is electron deficient.

(c) The metal-carbon bond of fischer carbene has relatively high rotational barrier.

(d) The metal atom of fischer carbene is relatively electron rich.

3. How many carbene unit in the given complex have?



(a) 1 (b) 2 (c) 4 (d) 0

4. Match the following

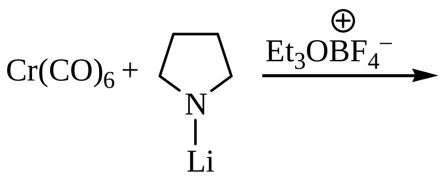
Column I	Column II
(I) Fischer carbene	(A) it behave like phosphorous ylide in some of its reaction.
(II) Shrocks carbene	(B) The carbene carbon is nucleophilic in nature.
	(C) The metal atom is relatively electron rich.
	(D) The Grubb's first generation catalyst is typical example for this

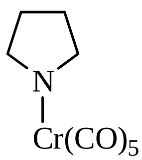
(E) It quite often does not obey the 18e$^{\ominus}$ rule.

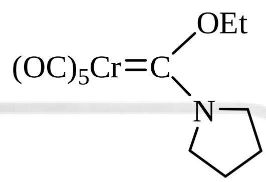
(F) The metal-carbon bond has relatively low rotational behaviour.

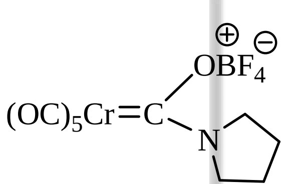
(a) I – C, F; II- B, D, E
(b) I – C, D; II – A, B, E
(c) I – C, F; II – A, B, E
(d) I – C, F; II- A, B, C, D

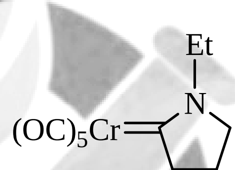
5. The product formed in the following reaction is:



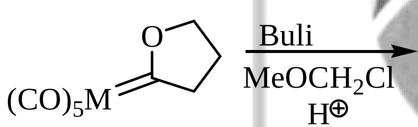
(a) 

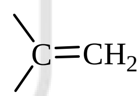
(b) 

(c) 

(d) 

6. The by product formed of the following reaction is



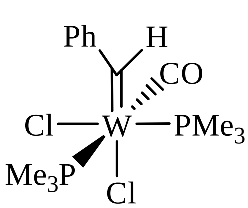
(a) MeOH
(b) CH_3COOH
(c) $PhCH_2OMe$
(d) 

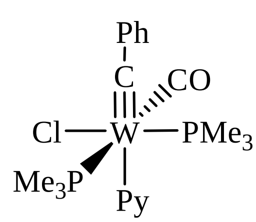
7. The product will be of the following reaction is:

$[Mn(CO)_5(CF_2)]^+ + H_2O \rightarrow$

(a) $[Mn(CO)_5(OH)]$
(b) $[Mn(CO)_5 = CF]$
(c) $[Mn(CO)_6]^+$
(d) $[Mn(CO)_6]$

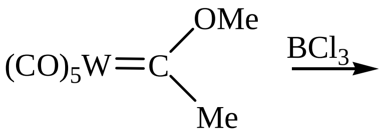
8. Which of the following complex gives higher stretching.

(I) 

(II) 

(a) I
(b) II
(c) I = II
(d) not define

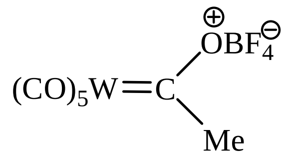
9. What will be the product(s) in the following reactions:



(a) $[(OC)_5W \equiv (Me\ ]^{+}\ BCl_4^{-}$

(b) $Cl(OC)_4W$ º (Me

(c) $RC \equiv CR$

(d) 

10. How many number of carbon monoxide are eliminated of the following reaction:

$Co(CO)_8 + HC \equiv CH \rightarrow (H_2C_2)\ Co_2(CO)_6 + CO$

(a) 2 (b) 4 (c) 3 (d) 8

11. Which one of the following statement is true for $[MLn(CR_2)$ complex, in which M = transition metal; L = Ligand; CR_2 = fischer carbene?

(a) L is a non-π-acceptor type

(b) R group is non-π-donor type

(c) Carbon centre is electrophilic in its reactivity

(d) Metal atom is in its high formal oxidation state

12. $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 give a compound X. X is represented as

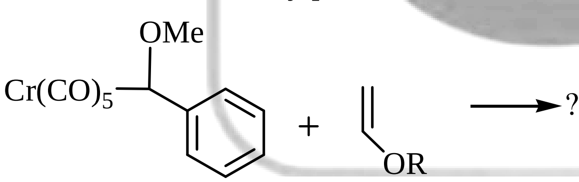
(a) WMe_6

(b) $(CO)_5W - Me$

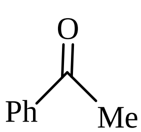
(c) $(CO)_5W = C(Me)\ (OMe)$

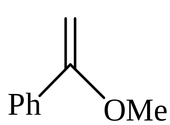
(d) $(CO)_5W \equiv CMe$

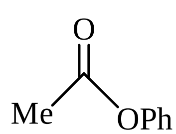
13. What will be the this by products of the following reaction:



(Carbon nucleophile)

(a) 

(b) 

(c) 

(d) MeOH

14. Which of the following catalyst is intermediate in between fischer and schrock types carbene.

(a) Wilkinson’s catalyst

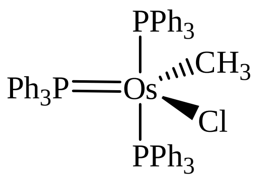
(b) Vaska’s complex

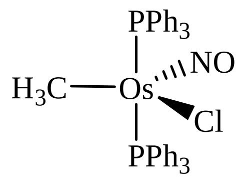
(c) Zeise's salt

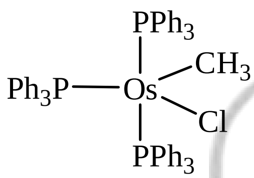
(d) Grubbs first generation catalyst

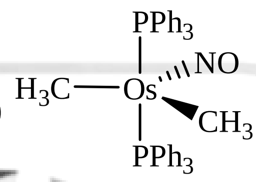
15. What will be the product of the following reaction:

$$Os(PPh_3)Cl(NO) \xrightarrow{CH_2N_2}$$

(a) 

(b) 

(c) 

(d) 

ANSWERS

1. (b)	6. (a)	11. (c)
2. (c)	7. (c)	12. (c)
3. (a)	8. (a)	13. (b)
4. (c)	9. (b)	14. (d)
5. (b)	10. (a)	15. **(a)**

HINT & SOLUTIONS

1. (b)

Sol. In fischer carbene the carbene is electron deficient, attacked by nucleophiles & stabilized by heteroatom.

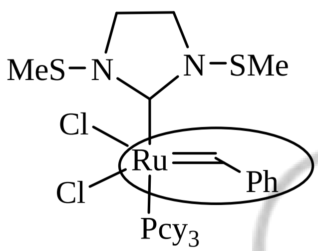
In schrock carbene, the carbene carbon is electron rich and attack by electrophile.

2. (c)

Sol. The metal-carbon bond of fischer carbene has a relatively low rotational barrier.

3. (a)

Sol.



There is one carbene unit in the given complex.

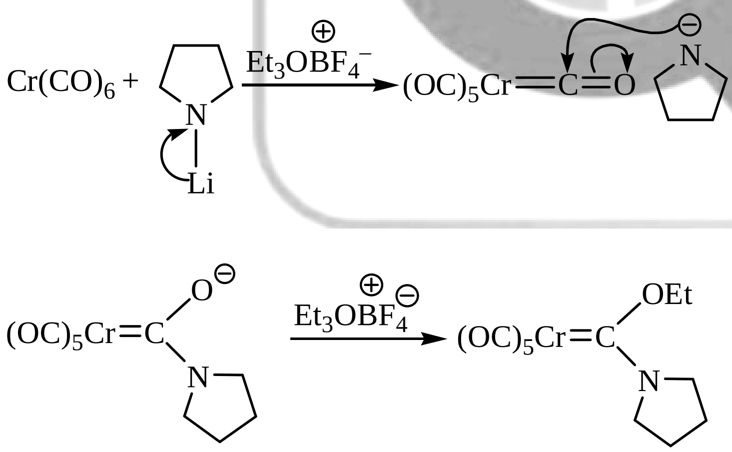
4. (c)

Sol. In fischer carbene metal atom is relatively electron rich & metal carbon bond has relatively low rotational barrier.

In schrocks carbene it behave like phosphorus ylide in some of its reaction, in this carbene carbon is nucleophilic in nature and it does not obey $18e^{\ominus}$ rule.

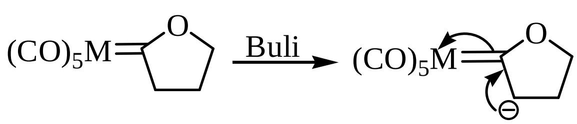
5. (b)

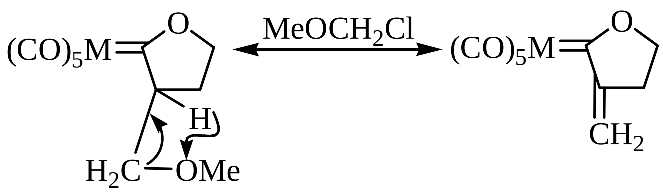
Sol.



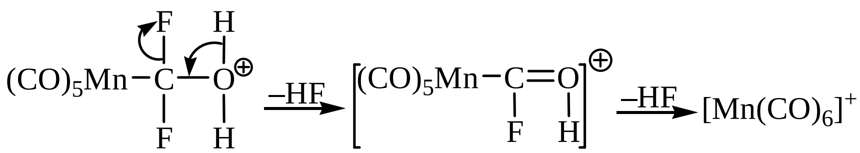
6. (a)

Sol.





7. (c)

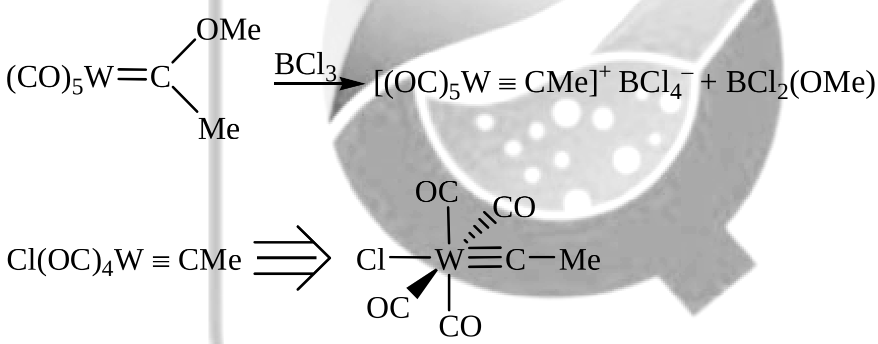
Sol. 

Here, the CF_2 carbene is electronically similar to a fischer carbene because of the presence of fluorines, the carbon of CF_2 undergoes nucleophilic attack by water. The intermediate eliminates two HF molecules to give the molybdenum carbonyl complex.

8. (a)

Sol. The fact that the carbonyl stretching frequency in lower in the carbyne complex indicates that the electron density is more on the metal and the back donation to CO is higher. This means that the carbynes are better donor than the carbenene.

9. (b)

Sol. 

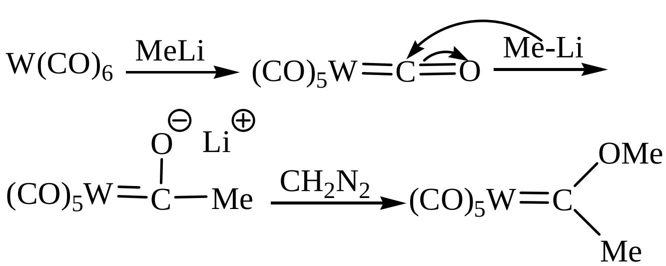
10. $Co(CO)_8 + HC \equiv CH \rightarrow (H_2C_2)\ Co_2(CO)_6 + 2CO$

When alkyne present in bridged position, then it will donate $4e^{\ominus}$. So in this reaction there will be replacement of 2CO, which is $4e^{\ominus}$ donar.

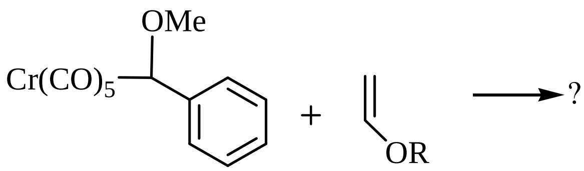
11. (c)

Sol. Because carbene carbon is electrophilic in nature, in fischer carbene ligand is π-acceptor and R group is π-donar and metal in low oxidation sate will be present.

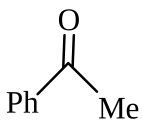
12. (c)

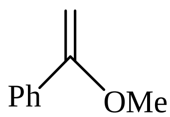
Sol. 

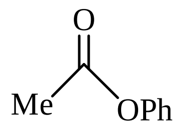
13. What will be the this by products of the following reaction:



(Carbon nucleophile)

(a) 

(b) 

(c) 

(d) MeOH

14. Which of the following catalyst is intermediate in between fischer and schrock types carbene.

(a) Wilkinson's catalyst

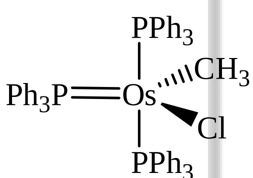
(b) Vaska's complex

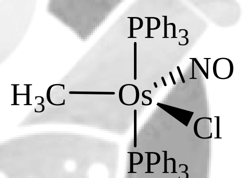
(c) Zeise's salt

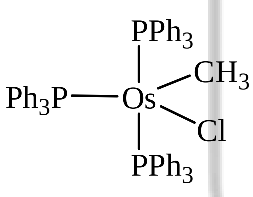
(d) Grubbs first generation catalyst

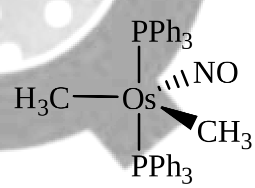
15. What will be the product of the following reaction:

$$Os(PPh_3)Cl(NO) \xrightarrow{CH_2N_2}$$

(a) 

(b) 

(c) 

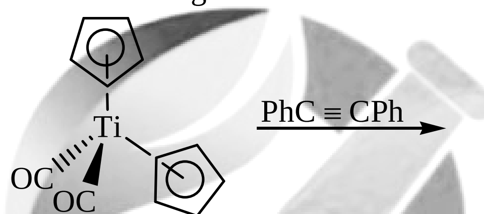
(d) 

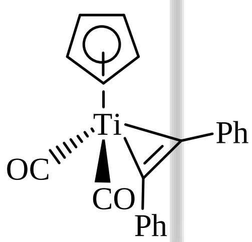
xxxxx

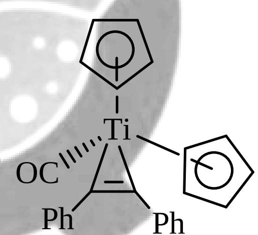
DPP- 12 OMC

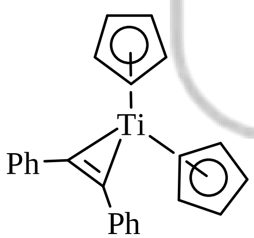
1. The addition of an alkyne to $Co_2(CO)_8$ results in the formation of a Co_2C_2 cluster in which the alkyne C–C bond length is
(a) longer than free alkyne
(b) shorter than free alkyne
(c) equal to the free alkyne
(d) can't predict

2. Suggest possible product of the following reaction :



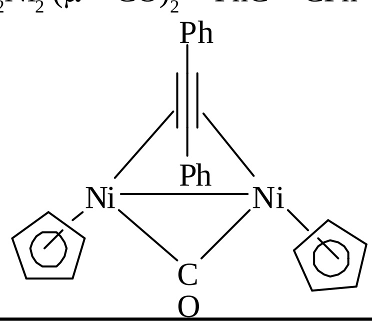
(a)


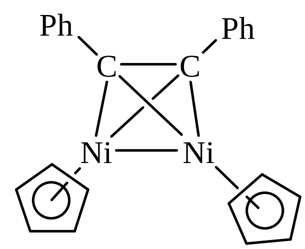
(b)


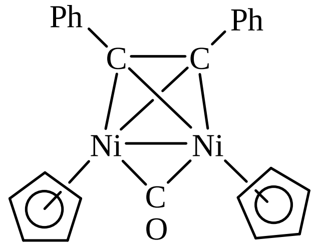
(c)


(d) No reaction

3. Product of the following reaction
$Cp_2Ni_2\ (\mu - CO)_2 + PhC \equiv CPh \longrightarrow$

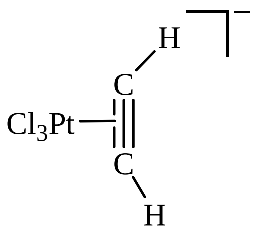
(a)


(b)


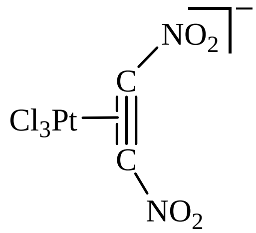
(c) 

(d) No reaction

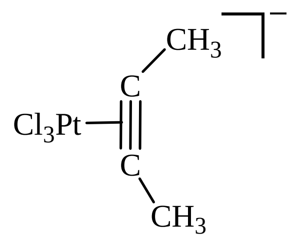
4. Correct bond length order of M-alkyne in the given complexes.



(i)



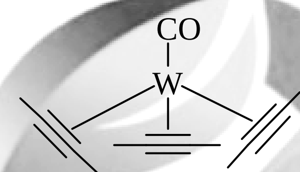
(ii)



(iii)

(a) (i) > (ii) > (iii) (b) (iii) > (ii) > (i) (c) (i) > (iii) > (ii) (d) (iii) > (i) > (ii)

5. The electron count of alkyne following $18e^-$ rule in the given complex will be



(a) All 3 alkyne will give $2e^-$ count.

(b) 1 alkyne will give $2e^-$-count and other 2 alkyne will give $4e^-$-count.

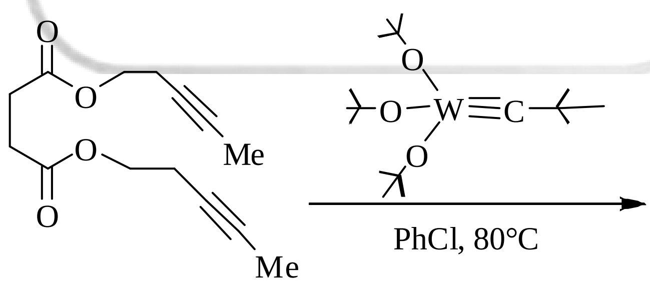
(c) 2 alkyne will give $2e^-$ count and 1 will give $4e^-$ count.

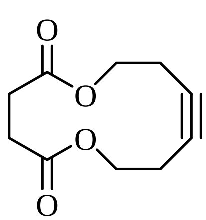
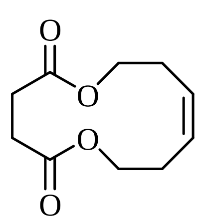
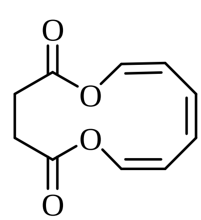
(d) All 3 alkyne will give $4e^-$-count.

6. When alkyne is bridged with 2 metals what will be the electron count of alkyne.

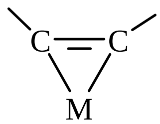
(a) 2 (b) 4 (c) 3 (d) None

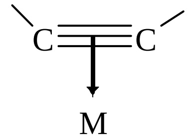
7. Product of the given reaction will be

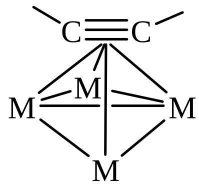


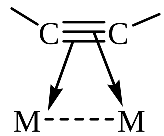
(a)  (b)  (c)  (d) No reaction

8. Identify the ones which is not a co-ordination mode of alkyne ligand.

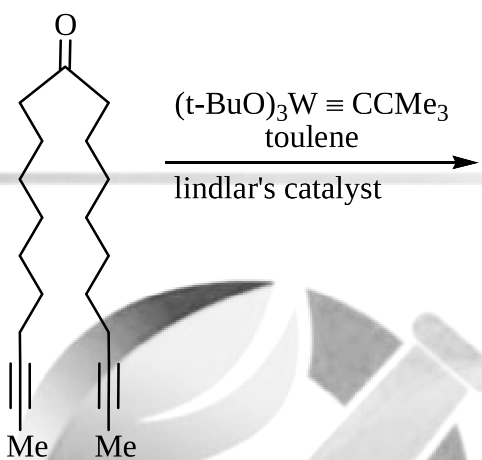
(a) 

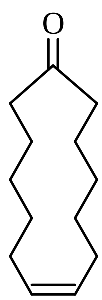
(b) 

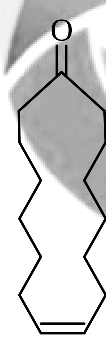
(c) 

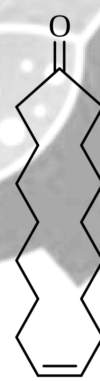
(d) 

9. The product of the given alkyne metathesis is



(a) 

(b) 

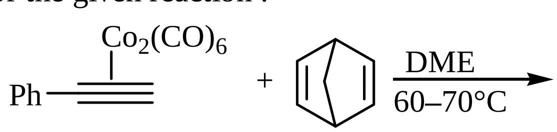
(c) 

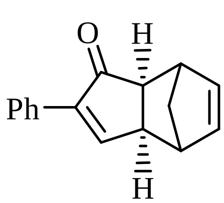
(d) No reaction

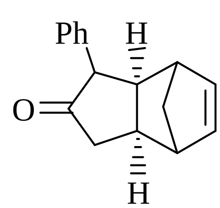
10. Metal alkyne complex mainly exist as Metallocycloproton

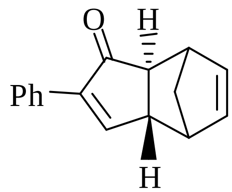
(a) due to high electronegativity of C
(b) due to C-C triple bond.
(c) due to metal atom
(d) due to structure of alkyne

11. Predict the product for the given reaction :



(a) 

(b) 

(c) 

(d) No reaction

12. Applications of alkyne metathesis are

(a) synthesis of polymers

(b) electronically interesting macrocycles

(c) Natural products

(d) All of these

13. Alkynes coordinate for more readily than alkenes to a metal due to

(a) steric reason

(b) electronic reason

(c) less electronegativity

(d) both (a) and (c)

×××××

ANSWERS

1. (a)
2. (b)
3. (b)
4. (d)
5. (b)
6. (b)
7. (a)
8. (c)
9. (c)
10. (a)
11. (a)
12. (d)
13. (d)

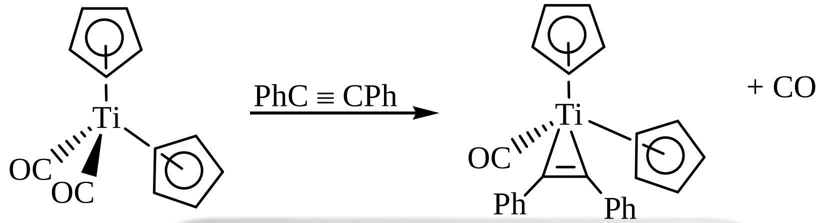
HINT & SOLUTIONS

1. (a)

Sol. The addition of an alkyne to $Co_2(CO)_8$ results in the formation of a Co_2C_2 cluster in which the alkyne C–C bond is lengthened to 136 pm and the bond length in free alkyne is 120 pm.

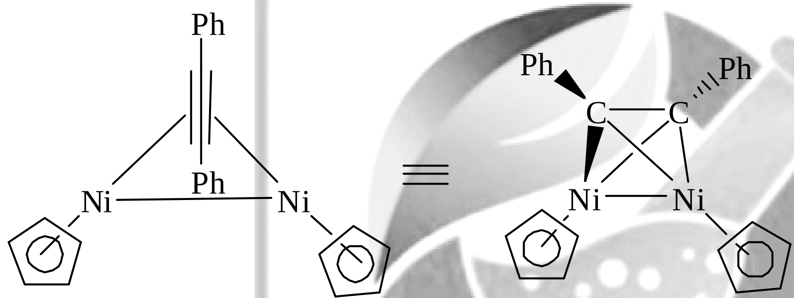
2. (b)

Sol. Substitution of CO by an alkyne. The π-bonded alkyne acts as $2e^-$ donor. The Ti centre retains an 18 e^- count.



3. (b)

Sol. $Cp_2Ni\ (\mu - CO)_2 + Ph\ C \equiv CPh \longrightarrow$

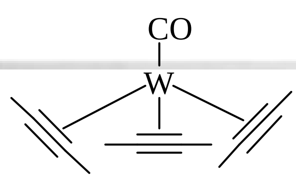


4. (d)

Sol. As we know the presence of EWG enhance the π-back bonding so in (ii) NO_2 is EWG due to which M-alkyne will have stronger bond and lesser bond length.

$\therefore$ The order of M-alkyne bond length will be (iii) > (i) > (ii).

5. (b)

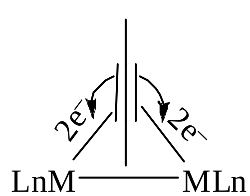


TEC = 6 + 2 + 2 + 4 + 4

= $18e^-$

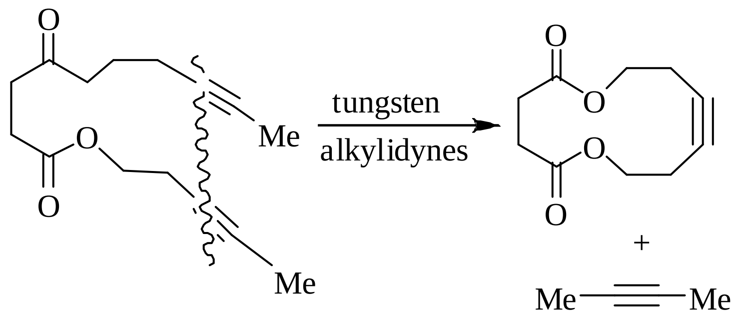
6. (b)

Sol. Alkyne act as $4e^-$-donor. It uses one π-bond to one metal and other π-bond to other metal.



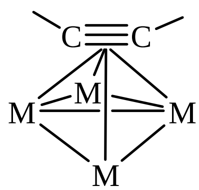
7. (a)

Sol.



8. (c)

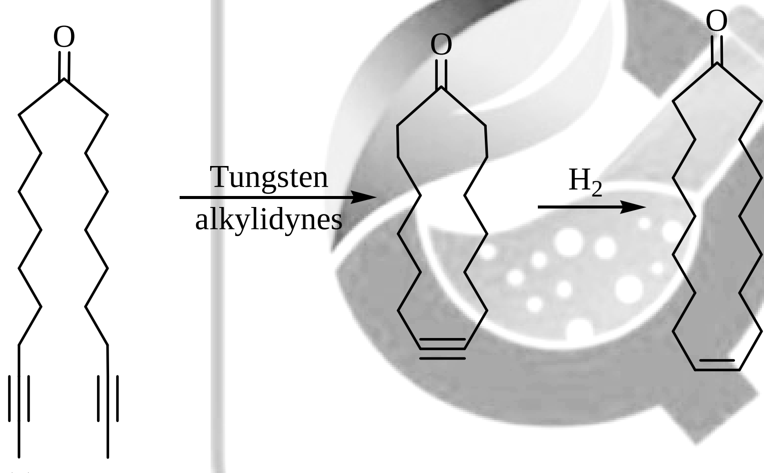
Sol.



This bonding is not a co-ordination mode of an alkyne ligand.

9. (c)

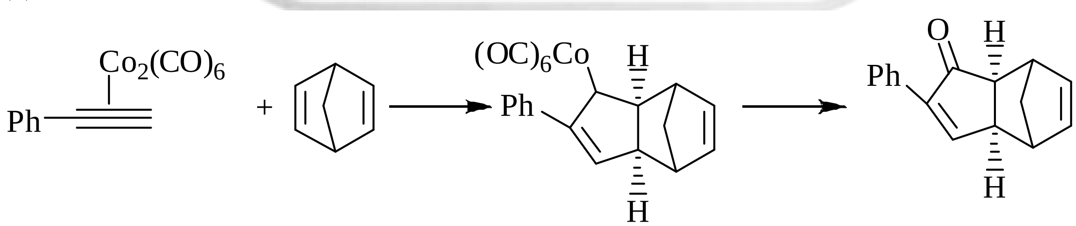
Sol.



10. (a)

11. (a)

Sol.



12. (d)

13. (d)

Sol. Alkynes coordinate far more readily than alkenes due to steric (more open, less hindered) and electronic (better donor, 2 or 4 e-bonding) reasons.

×××××

QUANTA CHEMISTRY

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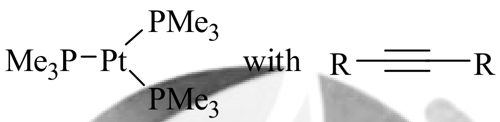
CSIR-NET|IIT-GATE|IIT-JAM |Other Msc. Entrance

DPP- 13 OMC

1. The square planar complex $[IrCl(PPh_3)_3]$ undergoes oxidative addition of Cl_2 to give two products

   (a) fac and mer (b) cis and trans (c) enantiomers (d) linkage isomerism

2. Below reaction is an example of?



   (a) reductive elimination (b) oxidative addition

   (c) migratory insertion (d) None of the above

3. The correct reactivity order for Ni(0) complexes with Mel is:-

   (a) $Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PR_3)_2$(alkene) $> Ni(PAr_3)_2$(alkene)

   (b) $Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PAr_3)_2$(alkene) $> Ni(PR_3)_2$(alkene)

   (c) $Ni(PAr_3)_2$(alkene) $> Ni(PR_3)_2$(alkene) $> Ni(PAr_3)_4 > Ni(PR_3)_4$

   (d) $Ni(PAr_3)_4 > Ni(PAr_3)_2$(alkene) $> Ni(PR_3)_4 > Ni(PR_3)_2$(alkene)

4. Correct order of reactivity of complexes with HCl is

   (a) $IrCl(CO)(PPh_3)_2 > IrCl(CO)(PMe_3)_2 > IrMe(CO)(PMe_3)_2 > IrPh(CO)(PMe_3)_2$

   (b) $IrCl(CO)(PMe_3)_2 > IrCl(CO)(PPh_3)_2 > IrMe(CO)(PMe_3)_2 > IrPh(CO)(PMe_3)_2$

   (c) $IrMe(CO)(PMe_3)_2 > IrPh(CO)(PMe_3)_2 > IrCl(CO)(PMe_3)_2 > IrCl(CO)(PPh_3)_2$

   (d) $IrPh(CO)(PMe_3)_2 > IrMe(CO)(PMe_3)_2 > IrCl(CO)(PMe_3)_2 > IrCl(CO)(PPh_3)_2$

5. The oxidative – addition reaction is more favourable for the complex containing –

   (a) Fe(0) (b) Co(I) (c) Ni(II) (d) Fe(II)

6. On oxidative addition of O_2 to $Ir(CO)(Cl)(PPh_3)_2$, the oxidation state and co – ordination number of Ir changes, respectively by –

   (a) 1 and 3 (b) 2 and 2 (c) 3 and 1 (d) 2 and 3

7. In oxidative addition reactions alkene, alkynes and O_2 are the examples of:

   (a) electrophilic substrate

   (b) non-electrophilic substrate

   (c) addition substrate

   (d) intact substrate

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8. Reactions A and B are termed as respectively –

$$1.\ SnCl_2 + Co(CO)_4 \longrightarrow (OC)_4Co-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Sn}}-Co(CO)_4$$

$$2.\ Me_2SnCl_2 + 2NaRe(CO)_5 \longrightarrow (OC)_5Re-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Sn}}-Re(CO)_5 + 2NaCl$$

(a) Insertion, Metathesis (b) Metathesis, insertion
(c) Oxidative addition, Metathesis (d) Oxidative addition, insertion

9. Intact substrates are
I. oxidative addition substrates
II. reductive elimination substrates
III. double or triple bond is must
IV. double or triple bond electronegative
The correct answer is:
(a) I and III only (b) III only (c) I and IV only (d) I, II and III only

10. Intact substrates for oxidative addition
(A) two separate anionic ligands are formed oxidative addition
(B) only one of the n – bond is broken leaving a – intact
(C) ligand pricks up two electrons from metal becomes dianionic
(D) electron donating groups on alkenes e oxidative process
(a) Only A (b) B and C (c) A and B (d) C and D

11. Presence of empty orbitals on the metal centre in order to perform oxidative addition is generally required in
(A) non – electrophilic substrates (B) electrophilic substrates
(C) intact substrates (D) All of the above
(a) A and C (b) B and C (c) A and D (d) C and D

12. In oxidative addition of $Ir(Co)(PPh_3)PPh_3Cl$ by CH_3Br, the starting material is
(a) 18 e^- (b) 16 e^- (c) 17 e^- (d) 15 e^-

13. The product (P) formed in the following reaction is?
$[\eta^5 - CpRh\ (CO)_2] + CF_3CF_2I \rightarrow (P)$
(a) cis $[(\eta^5 - Cp)Rh(CO)_2(CF_3CF_2)(I)]$ (b) cis $[(\eta^5 - Cp)Rh(CO)(CF_3CF_2)(I)]$
(c) Trans $[(\eta^5 - Cp)Rh(CO)_2(CF_3CF_2)(I)]$ (d) Trans $[(\eta^5 - Cp)Rh(CO)(CF_3CF_2)(I)]$

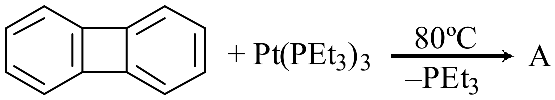
14. Choose the correct order of rate of oxidative addition in following pairs.
(a) $[Rh(PPh_3)_2Cl] > [Rh(PPh_3)COCl]$; $[Co(dppe)_2]^+ > [Ir(dppe)_2]^+$
(b) $[Rh(PPh_3)_2Cl] < [Rh(PPh_3)COCl]$; $[Co(dppe)_2]^+ < [Ir(dppe)_2]^+$
(c) $[Rh(PPh_3)_2Cl] > [Rh(PPh_3)COCl]$; $[Co(dppe)_2]^+ < [Ir(dppe)_2]^+$
(d) $[Rh(PPh_3)_2Cl] < [Rh(PPh_3)COCl]$; $[Co(dppe)_2]^+ > [Ir(dppe)_2]$

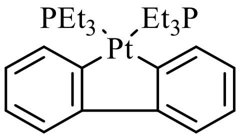
15. Which of the following compounds will not undergo oxidative addition of methyl iodide.

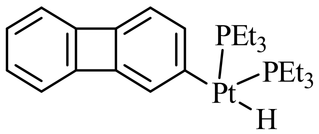
(a) $[Ir(PPh_3)_2COCl]$ (b) $[RhI_2(CO)_2]^{-1}$

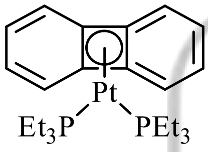
(c) $[(\eta^5 - Cp)_2Ti(Me)Cl]$ (d) Both (b) and (c)

16. Predict the product (A) formed in the following reaction.



(a  , oxidative addition on C – C bond

(b)  , oxidative addition on C – H bond

(c)  , oxidative addition on C – C bond

(d) none of these

17. Which one of the following will NOT undergo oxidative addition by methyl iodide?

(a) $[Rh(CO)_2I_2]^-$ (b) $[Ir(PPh_3)_2(CO)Cl]$ (c) $[\eta^5 - CpRh(CO)_2]$ (d) $[\eta^5 - Cp_2Ti(Me)Cl]$

18. The typical electronic configurations of the transition metal centre for oxidative addition

(a) d^0 and d^8 (b) d^5 and d^8 (d) d^8 and d^{10} (d) d^5 and d^{10}

19. The compound that undergoes oxidative addition reaction in presence of H_2 is **(NET Dec. 2014)**

(a) $[Mn(CO)_5]^-$ (b) $[(\eta^5 - C_5H_2]TiMeH$

(c) $[lrCl(CO)(PPh_3)_2]$ (d) $[(\eta^5 - C_5H_5)_2ReH]$

20. The reaction of phosphorus trichloride with phenyllithium in 1:3 molar ratio yields product 'A', which on further treatment with methyl iodide produces 'B'. The reaction of B with 'BuLi gives product 'C'. The products A, B and C, respectively, are

(a) $[PPh_4]Cl, [Ph_2P{=}CH_2]I, Ph_2P(^nBu)$ (b) PPh_3, $[Ph_3PI]Me$, $Ph_2P(^nBu)_3$

(c) PPh_3, $[Ph_3PMe]I$, $Ph_3P = CH_2$ (d) $[PPh_4]Cl$, $[Ph_3P{=}CH_2]I$, $[Ph_3P(^nBu)]Li$

×××××

ANSWERS

1. a	2. b	3. a	4. c	5. a	6. b	7. d	8. a	9. a	10. b	11. a	12. b
13. d	14. c	15. c	16. a	17.d	18.c	19.c	20.c				

QUANTA CHEMISTRY

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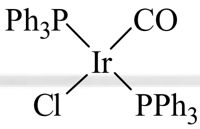
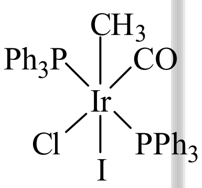
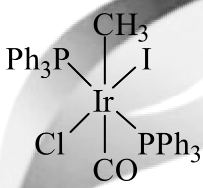
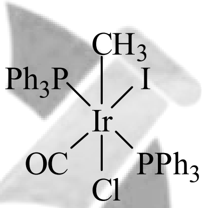
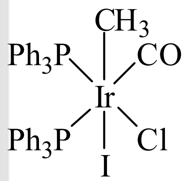
DPP- 14 OMC

1. Identify the product in the reaction between  and CH_3I going at room temperature via S_N2 mechanism

(a)  (b)  (c)  (d) 

2. For the reaction of trans – $[IrX(CO)(PPh_3)_2]$ (X = F, Cl, Br, I) with O_2, correct order of variation of rate with X is

(a) Br > I > F > Cl (b) F > Cl > Br > I (c) F ≈ Cl ≈ Br ≈ 1 (d) I > Br > Cl > F

3. Which of the following statement is not true

(a) For oxidative addition metal should be co – ordinatively unsaturated.

(b) There should be suitable orbitals available for bond formation

(c) There should not be bonding electron density on the metal

(d) Oxidative addition increases on moving down the group.

4. The product(s) of the reaction of $[IrCl(CO)(PC_6H_5)_3)_2]$ and CH_3I is /are

(a) $[IrCl(COCH_3)I(PPh_3)_2]$ (b) $[IrCl(CO)(CH_3)I(PPh_3)_2]$

(c) $[Ir(CO)(PPh_3)_2]+CH_3Cl$ (d) $[IrCl(CO)(CH_3)I(PPh_3)]+PPh_3$

5. On oxidative addition of O_2 to $Ir(CO)Cl(PPh_3)_2$, the oxidation state and coordination number of Ir changes, respectively, by

(a) 1 and 3 (b) 2 and 2 (c) 3 and 1 (d) 2 and 3

6. The reaction of $Co_2(CO)_8$ with sodium amalgam followed by methyl iodide leads to formation of

(a) $Me_3(CO)_3Co$ (b) $(MeCO)_3Co(CO)_3$

(c) $MeCo(CO)_4$ (d) $MeCo(CO)_4I$

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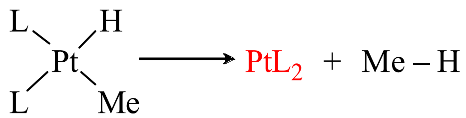
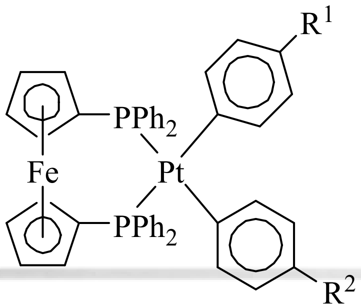
7. Find rate of reductive elimination in the following complex?



(I) L = PMe_3 (II) L = PMe_2Ph (III) L = $PMePh_2$

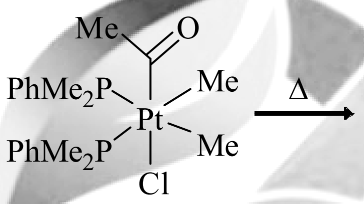
(a) III > II > I (b) III > I > II (c) II > III > I (d) None

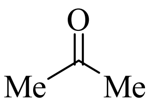
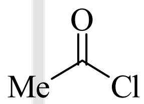
8. Find the rate of reductive elimination



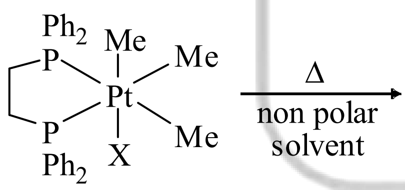
(a) $R^1 = R^2 = CHO$ (b) $R^1 = R^2 = OMe$ (c) $R^1 = OMe$, $R^2 = NO_2$ (d) None

9. Find the product of reductive elimination



(a)  (b) Me – Me (c) Me – Cl (d) 

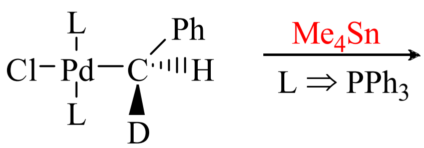
10. Find the product?

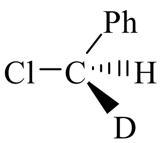
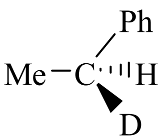
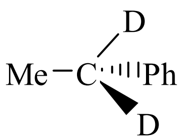


X = OAc

(a) Me – Me (b) Me – X (c) Me – H (d) None

11. Find the product of the reaction



(a)  (b)  (c)  (d) (b) & (c) both

12. Which of the following statement is true about reductive elemination?

(a) A vacant co – ordination site on metal centre is prerequisite

(b) Cis orientation of the participating ligands is must

(c) The more electron rich the centre, the more facial is the reaction

(d) Π donor on metals generally accelerate reductive elimination.

13. Find product A and B in the following reaction respectively.

$$(\eta^5-Cp)_2W(CH_3)(H) \xrightarrow{h\nu} A \xrightarrow[\Delta]{\text{Benzene}}$$

(a) $(\eta^5 - Cp)_2W$, $(\eta^5 - Cp_2W)(C_6H_6)$ (b) $(\eta^5 - Cp)_2WH$, $[(\eta^5 - Cp)_2W(Ph)(H)]$

(c) $(\eta^5 - Cp)_2W$, $[(\eta^5 - Cp)_2W(Ph)(H)]$ (d) $(\eta^5 - Cp)(\eta^5Cp)W$, $(\eta^5 - Cp_2)W(Ph)(H)_3)$

14. Consider the following statements

(1) Reductive elimination, the reverse of oxidative addition decreases both the oxidation state and coordination number by two.

(2) Oxidative coupling, like oxidative addition has oxidation state and co-ordination number both increase by two, but two new ligands are involved and a new bond is formed between them.

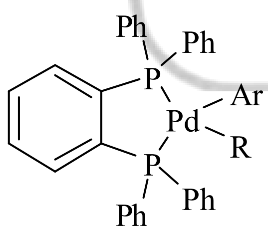
(3) The oxidative addition is usually favoured by strongly donor ligands because these ligand stabilize the oxidized state.

(4) $Fe(CO)_5 \xrightarrow[\text{(ii) } Me_3O^+]{\text{(i) } LiNEt_2} (OC)_4Fe{=}C(NEt_2)(OMe)$ (X) The product (X) is an example of Schrock carbene.

The correct statement is/are

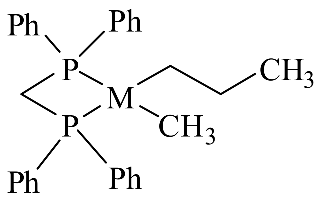
(a) 1, 2, 3 and 4 (b) 3 and 4 (c) 1, 2 and 3 (d) 4 only

15. The reductive elimination of Ar – R (coupled product) from A is facile when

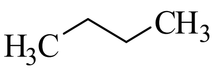
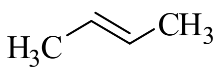
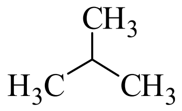
(A) 

(a) $R = CH_3$ (b) $R = CH_2Ph$ (c) $R = CH_2COPh$ (d) $R = CH_2CF_3$

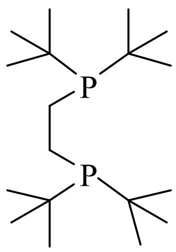
16. The least probable product from A on reductive elimination is

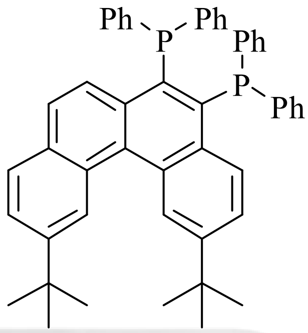


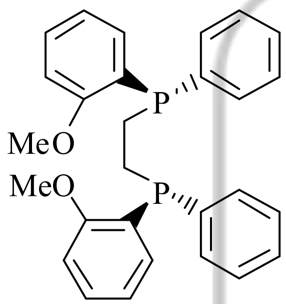
(A)

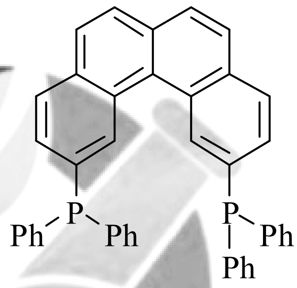
(a)  (b) CH_4 (c)  (d) 

17. In the complex [Pd(L-L)(Me)(Ph)], the bisphosphine(L-L) that does not allow reductive elimination of PhMe, is

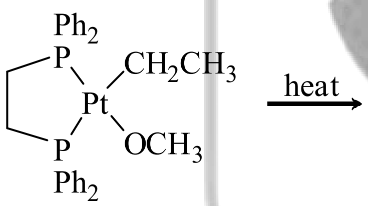
(a) 

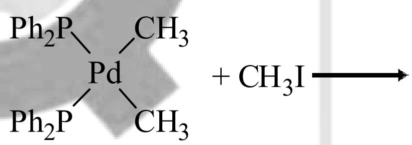
(b) 

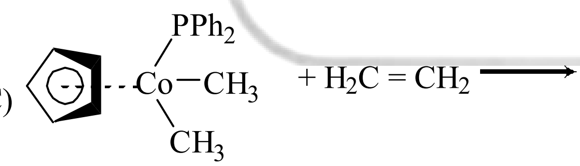
(c) 

(d) 

18. Consider the following reactions:

(A) 

(B) 

(C) 

The reaction (s) which will NOT produce ethane as a product is/are

(a) A (b) B (c) C (d) A and C

19. The oxidative addition and reductive elimination steps are favoured by

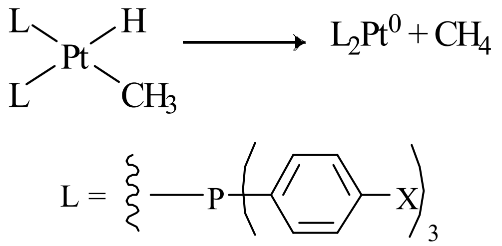
(a) Electron rich metal centres

(b) Electron deficient metal centers

(c) Electron deficient and electron rich metal centers respectively

(d) Electron rich and electron defined metal centers respectively

20. Predict the relative rates for the following reductive elimination for H, Cl, CH_3, OCH_3



(a) $Cl > H > CH_3 > OCH_3$

(b) $H > Cl > OCH_3 > CH_3$

(c) $OCH_3 > CH_3 > H > Cl$

(d) $CH_3 > H > Cl > OCH_3$

×××××

ANSWERS

1. a	2. d	3. c	4. b	5. b	6. c	7. a	8. c	9. a	10. b	11. d
12. b	13. b	14. c	15. a	16. c	17. d	18. a	19. d	20. a		

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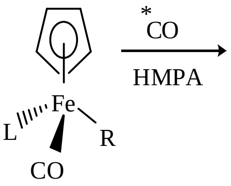
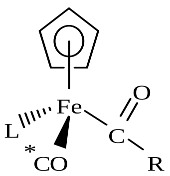
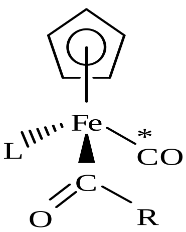
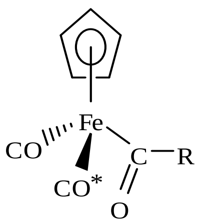
1. Find the major product?



(a) 

(b) 

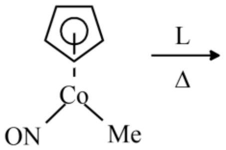
(c) 

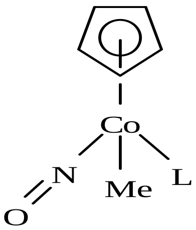
(d) None

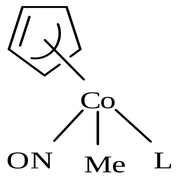
2. Find the order of migratory insertion reaction

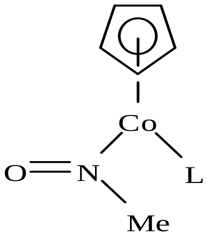
(a) 3d > 4d > 5d (b) 3d > 5d > 4d (c) 5d > 4d > 3d (d) None

3. Find the major product of the reaction



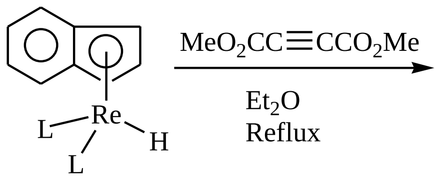
(a) 

(b) 

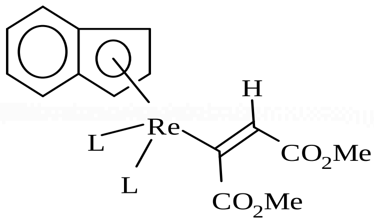
(c) 

(d) None

4. Find the major product



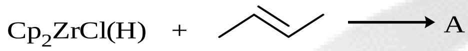
(a) Migratory insertion reaction take place

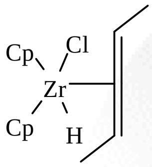
(b) 

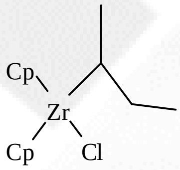
(c) (a) and (b) both

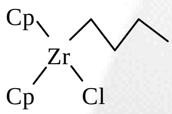
(d) None

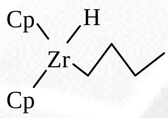
5. The final product(A) in the following reaction of alkene isomerisation



(a) 

(b) 

(c) 

(d) 

6. The final product of [Cp^*_2Th H(OR)] with CO at –78ºC

(a) $(\eta^5-C_5Me_5)_2(OR)Th \leftarrow \overset{O}{\overset{||}{C}}-H$

(b) $(\eta^5-C_5Me_5)_2(OR)Th-\overset{O}{\overset{||}{C}}-H$

(c) $(\eta^5-C_5Me_5)_2HTh-\overset{O}{\overset{||}{C}}-OR$

(d) $(\eta^5-C_5Me_5)_2HTh \leftarrow \overset{O}{\overset{||}{C}}-OR$

7. Which of the following statement is correct about the reaction, when $[Cp_2Fe]^+$ is added to the given reaction

$$\left[MeFe(Cp)(CO)(PPh_3)\right]+CO \xrightarrow[Cp_2Fe^+]{} (MeCO)Fe(Cp)(CO)(PPh_3)$$

(a) Rate of reaction decreases

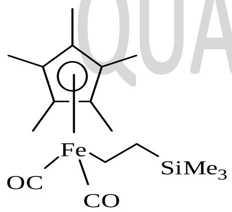
(b) Rate of reaction increases

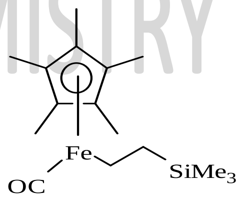
(c) Rate of reaction does not affected

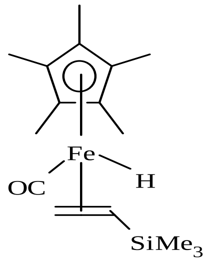
(d) Cannot predict

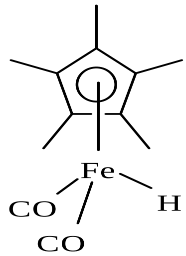
8. The major product formed in the following reaction is

$$Cp^*Fe(CO)_2SiMe_3 \xrightarrow[C_2H_4]{h\nu} A$$

(a) 

(b) 

(c) 

(d) 

9. The major product formed in the following reaction is

$MeFe(NO)(CO)_3 + CO \rightarrow A$

(a) $[MeC(O)]Fe(NO)(CO)_3$ (b) $[MeN(O)]Fe(CO)_{4\backslash}$

(c) $MeFe(NO)(CO)_4$ (d) $[MnFe(CO)_4]^{-1}$

10. The following reaction $[RhI_3(CO)_2CH_3]^- \rightarrow [RhI_3(CO)(Solvent)(COCH_3)]^-$ is

(a) oxidative addition (b) migratory insertion

(c) reductive elimination (d) simple addition reaction

11. Which of the following statement is incorrect about migratory insertion.

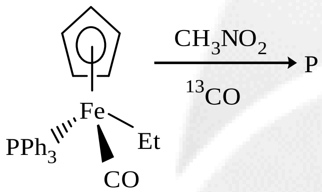
(a) During migratory insertion there is no change in the formal oxidation state of metal

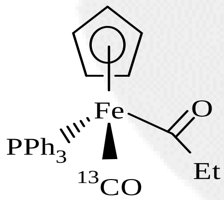
(b) If migratory ligand is chiral than the reaction usually proceeds with retention of configuration at that chiral carbon

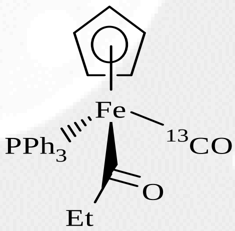
(c) The bulky ligand coordinated to the metal will enhance the rate of migratory insertion

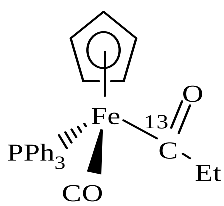
(d) none of these

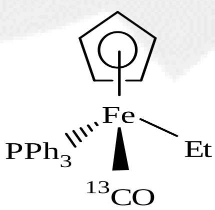
12. Find the major product P.

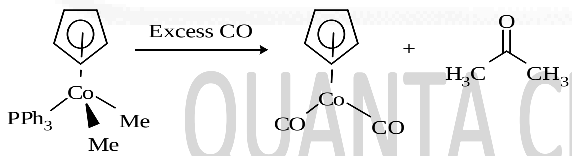


(a) 

(b) 

(c) 

(d) 

13. 

The most plausible sequence of mechanistic step for the above reaction is

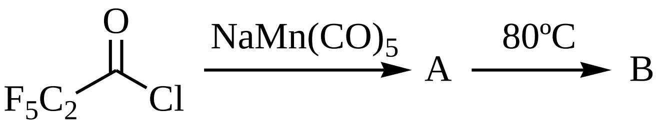
(a) (i) loss of PPh_3 (ii) addition of CO(iii) addition of CO(iv) reductive elimination of acetone (v) addition of CO.

(b) (i) Loss of PPh_3(ii) addition of CO (iii) Insertion of CO (iv) addition of excess CO along with reductive elemination of acetone.

(c) (i) Addition of CO (ii) loss PPh_3 (iii) insertion of CO (iv) addition of CO (v) loss of PPh_3

(d) (i) Addition of CO (ii) insertion of CO (iii) reductive elimination of acetone (iv) addition of CO (v) loss of PPh_3.

14. The major product (P) formed in the following reaction



(a) $F_5C_2-\overset{O}{\overset{||}{C}}-Mn(CO)_5$ (b) $F_5C_2-Mn(CO)_5$

(c) $F_5C_2-\overset{O}{\overset{||}{C}}-Mn(CO)_4$ (d) $F_5C_2-\overset{O}{\overset{||}{C}}-Mn(CO)_3$

15. Which of the following statement is true about reaction A and B respectively

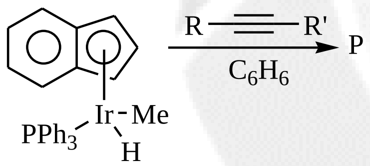
(A) $SnCl_4 + Co_2(CO)_8 \longrightarrow (CO)_4Co\,SnCl_2-Co(CO)_4$

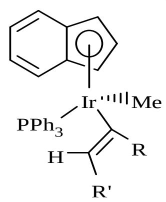
(B) $CpFe(PPh_3)(CO)Et \xrightarrow[13\ CO]{HMPA} {}^{13}CO(Ph_3P)CpFe\,(COOEt)$

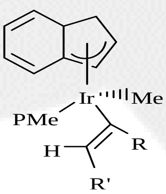
(a) Insertion, metathesis (b) Metathesis, insertion

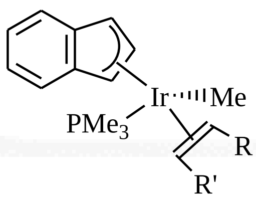
(c) Insertion, Insertion (d) Oxidative addition , Insertion

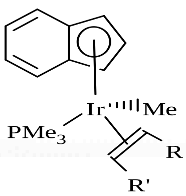
16. The major product in the following reaction is



(a)


(b)


(c)


(d)


17. Insertion reactions are usually favoured by:

(a) Electron rich metal centres (b) Electron deficient metal centres

(c) Empty d – orbitals on metal atom (d) None of the above

18. For migratory insertion reaction, what are constant can be extracted from rate data?

(a) Rate = $k_a[CO]$ (b) Rate = $k_a\,[RMn(CO)_5][CO]$

(c) Rate = $k_a\,[(COR)Mn(CO)_4]$ (d) Rate = $k_a[RMn(CO)_5]$

19. In which direction would you expect a late transition metal hydride to undergo insertion with $CH_2 = CF_2$ to give the most stable alkyl product?

(a) $M - CH_2 - CF_2H$ (b) $M - CF_2 - Me$

(c) $HCF_2 - M - Me$ (d) Both 1 and 2 will be stabilize the alkyl

20. Predict the products reaction from the following:

$CpRu(CO)_2Me + PPh_3 \rightarrow$

(a) $[CpRu(CO)(CO\ PPh_3)\ (Me)]$ (b) $[CuRu(CO)_2(Me)(PPh_3)]$

(c) $[CpRu(CO)(Me)(PPh_3)]$ (d) $[CpRu(CO)(COMe)(PPh_3)]$

×××××

ANSWERS

1. b	2. a	3. c	4. c	5. c	6. a	7. b
8. b	9. a	10. b	11. d	12. B	13. b	14. B
15. c	16. a	17. B	18. d	19. b	20. d	

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1. Predict the products reaction from the following:
$Mn(CO)_5CF_3 + CO \rightarrow$
(a) $[Mn(CO)_5(CF_3)CO]$ (b) $[Mn(CO)_5(CF_3CO)]$
(c) $[Mn(CO)_4(CF_3)CO]$ (d) No reaction

2. The product expected from the reaction between $[MnMe(CO)_5]$ and PPh_3 is-
(a) trans – $[Mn(Me)PPh_3(CO)_5]$ (b) trans – $[Mn(MeCO)(PPh_3)(CO)_4]$
(c) cis – $[Mn(MeCO)(PPh_3)(CO)_4]$ (d) cis – $[Mn(MeCO)(PPh_3(CO)_2]$

3. The product of the reaction between $CH_3Mn(CO)_5$ and ^{13}CO is –
(a) $(CH_3CO)Mn(CO)_5$ (b) $(^{13}CH_3CO)Mn(CO)_5$
(c) $(CH_3CO)Mn(^{13}CO)(CO)_4$ (d) $CH_3Mn(CO)_4$

4. The major product (P) in the above reaction

$$[CpFe(CO)(PPh_3)](Et) \xrightarrow[^{*}CO]{CH_3NO_2} (P)$$

(a) $[CpFe(\overset{O}{\overset{||}{C}}–Et)(^{*}CO)(PPh_3)]$ (b) $[CpFe(CO)(^{*}CO)(PPh_3)(Et)] + PPh_3$
(c) $[CpFe(^{*}\overset{O}{\overset{||}{C}}–Et)(CO)(PPh_3)]$ (d) $[CpFe(^{*}CO)(PPh_3)(Et)] + CO$

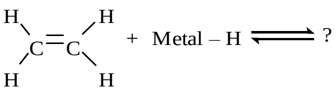
Directions (Q. 5 to 6):

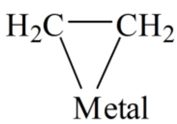
Migratory insertion reactions are those in which a cisoidal anionic and neutral ligands on the metal complex couples together to generate new coordinated anionic ligands. There is no change in oxidation state of d – electron count of metal centre and overall electron count on metal decreased by 2e.

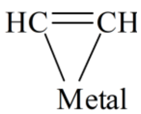
5. CO and alkyl migratory insertion reactions are also called
(a) substitution reactions (b) formyl reactions
(c) carbonylation reactions (d) addition elimination reactions

6. Insertion reactions is usually favoured by
(a) electron rich metal centres (b) electron deficient metal centres
(c) empty d – orbitals on metal atoms (d) None of the above

7. What is the product formed in the given reaction

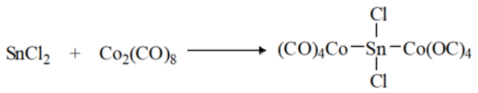


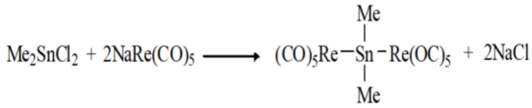
(a) $CH_3 – CH_2–M$ (b) 

(c) 

(d) None

8. Reactions A and B are, termed as respectively.

(A) 

(B) 

(a) Insertion, Metathesis (b) Metathesis, insertion

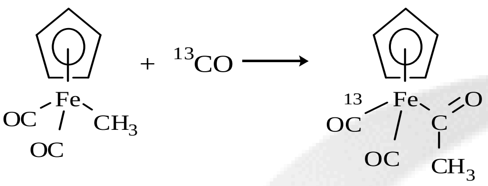
(c) Oxidative, addition, metathesis (d) Oxidative addition, insertion

9. The reaction, $[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5\ Mn\{C(O)Me\}]$ is an example for

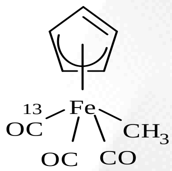
(a) oxidative addition (b) electrophilic substitution

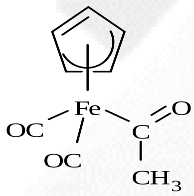
(c) nucleophilic substitution (d) migratory insertion

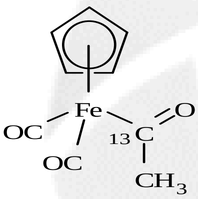
10. For the following reaction,

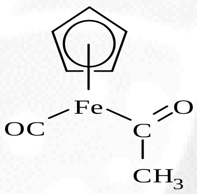


the structure of the intermediate is

(a) 

(b) 

(c) 

(d) 

11. Decarbonylation reaction of $[cis - (CH_3CO)Mn(^{13}CO)(CO)_4]$yields X, Y and Z where X = $[(CH_3)Mn(CO)_5]$; Y = $[cis\text{-}(CH_3)Mn(^{13}CO)CO_4]$; [Z = trans – $(CH_3)Mn(^{13}CO)(CO)_4]$. The molar ratio of the products (X : Y : Z) in this reaction is

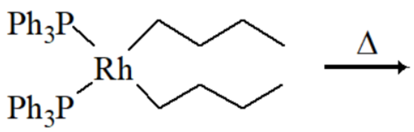
(a) 1 : 1 : 1 (b) 1 : 2 : 1 (c) 1 : 1 : 2 (d) 2 : 1 : 1

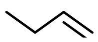
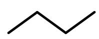
12. The product formed in the reaction of $MeMn(CO)_5$ with ^{13}CO is

(a) $(Me^{13}CO)\ Mn_2(CO)_5$ (b) $(MeCO)Mn(CO)_5$

(c) $(MeCO)Mn(CO)_4(^{13}CO)$ (d) $(Me^{13}CO)\ Mn(CO)_4(^{13}CO)$

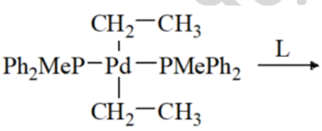
13. Find the product of the given reaction



(a)  (b) 

(c) C_8H_{18} (d) (a) and (b)

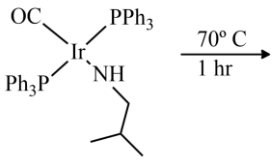
14. Find the product?

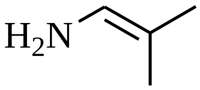


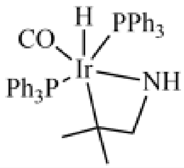
(a) $CH_2 = CH_2$ (b) $CH_3 - CH_3$

(c) $CH_3 - CH_2 - CH = CH_2$ (d) (a) and (b)

15. Find the product?



(a) 

(b) 

(c) None (d) Both

16. The most unstable species among the following is

(a) $Ti(C_2H_5)_4$ (b) $Ti(CH_2Ph)_4$ (c) $Pb(CH_3)_4$ (d) $Pb(C_2H_5)_4$

17. $Ru(C_2H_5)Cl(PPh_3)_2$ is stable only under a pressure of ethene because

(a) it is a 16 – electron complex

(b) it forms 18 electron adduct with ethene

(c) one of the decomposition product is ethene

(d) it prevents β – elimination of ethane

18. Which one of the following does not favour stabilization of metal – carbon bond?

(a) Chelation (b) Increased coordinate number

(c) β – elimination (d) Presence of π – acid ligands on the metal

19. What about $V(CH_2SiMe_3)_3$ and $Mn(CH_2CMe_3)_3$ is true?

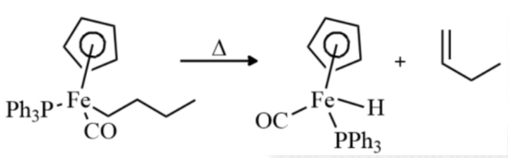
(a) Both are highly unstable organometallic compounds

(b) Both are stable organometallic compounds due to chelation

(c) Both are stable organometallic compounds due absence of β – elimination

(d) Metal neopentyls and trimethylsilylmethyles are stabilised due to the presence of β – elimination

20. The mechanistic step for the above given reaction is:



(a) Ligand dissociations, β – H transfer, ligand substitution

(b) β – H transfer, ligand substitution, ligand dissociation

(c) Ligand dissociation, ligand substitution, β – H transfer

(d) It is difficult to say what happen.

×××××

ANSWERS

1. d	2. c	3. c	4. a	5. c	6. b	7. a
8. a	9. d	10. b	11. b	12. c	13. d	14. d
15. a	16. a	17. d	18. c	19. c	20. c	

QUANTA CHEMISTRY

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DPP 17 – OMC

1. The most common pathway by which M–Et group (M = transition metal) decompose under anaerobic conditions is,

(a) α – H abstraction to given carbenes

(b) β – H abstraction to give olefin and M – H

(c) Facile generation of alkyl cations that react with water

(d) Formation of alkyl radicals that react with oxygen (a diradical)

2. Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)$, $Ti(i\text{-}Pr)_4$ and $TiEt_4$.

(Me = methyl, Ph = phenyl, i-Pr = isopropyl, Et = ethyl)

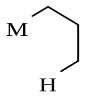
(a) $Ti(CH_2Ph)_4 < Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4$

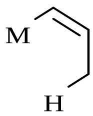
(b) $TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

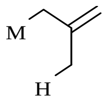
(c) $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)4$

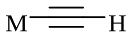
(d) $TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

3. The β – hydrogen elimination will be facile in

(a) 

(b) 

(c) 

(d) 

4. The following statements are given regarding the agnostic interaction C—H--Ir observed in $[Ir(Ph_3P)_3Cl]$.

(A) Up-field shift of C – H proton ^{1}H NMR spectrum

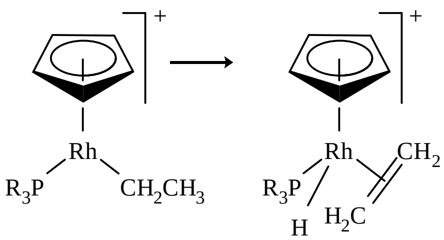
(B) Increased acid character of C – H

(B) $\nu_{C—H}$ in IR spectrum shifts to higher wavenumber

The correct answer is/are

(a) A and C (b) B and C (c) A and B (d) C only

5. The following transformation



is an example of

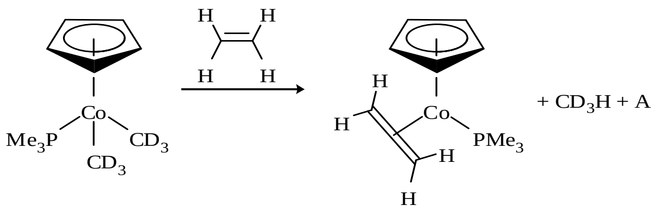
(a) oxidative addition

(b) insertion

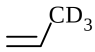
(c) β – hydride elimination

(d) reductive elimination

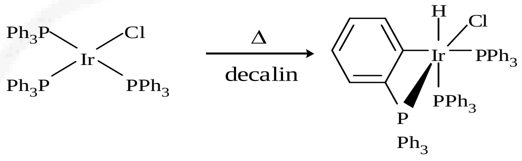
6. Product A in the following reaction is



(a) $D_2C = CD_2$ (b) $D_3C – CD_3$

(c)  (d) $H_2C = CD_2$

6. For the following reaction, correct statement(s) is/are



(I) (II)

(A) Oxidation state of iridium increases from I to III

(B) It is β – hydride elimination reaction

(C) I and II both are diamagnetic

(D) It is migratory insertion reaction

The correct answer is

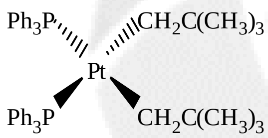
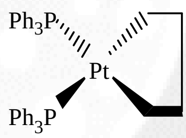
(a) A only (b) A and C (c) C and D (d) B, C and D

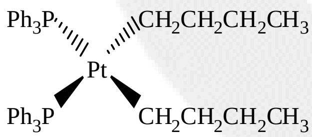
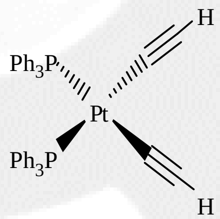
7. The correct order of thermal stability for the given compounds is

(a) $TiMe_4 > Ti(CH_2CMe_3)_4 > TiEt_4$ (b) $TiEt_4 > Ti(CH_2CMe_3)_4 > TiMe_4$

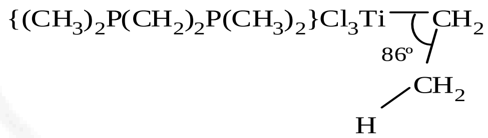
(c) $TiMe_4 > TiET_4 > Ti(CH_2CMe_3)_4$ (d) $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

8. Among the given platinum (II) complexes, the one that is thermally the most stable is

(a)  (b) 

(c)  (d) 

9. The bond angle (Ti – C – C) in the crystal structure of



is severely distorted due to

(a) hydrogen bonding interaction (b) agostic interaction

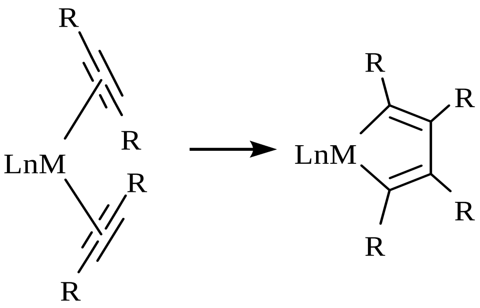
(c) steric bulk of the phosphine ligand (d) higher formal charge on metal

10. The following reaction is:

$$Mn_2(CO)_{10} + Br_2 \rightarrow 2MnBr(CO)_5$$

(a) reductive elimination (b) addition (c) insertion (d) oxidative addition

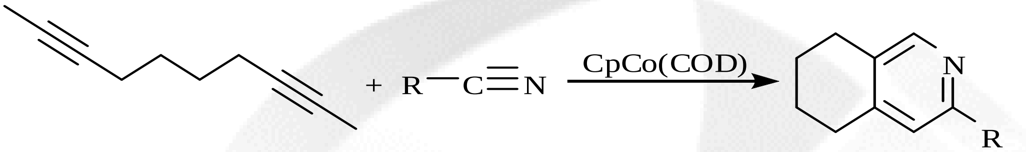
11 The following reaction is example of



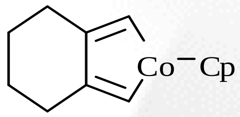
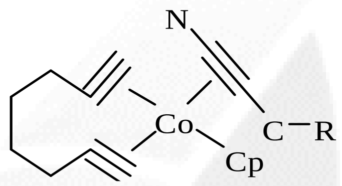
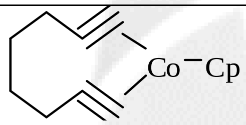
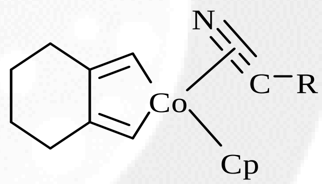
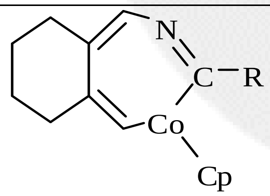
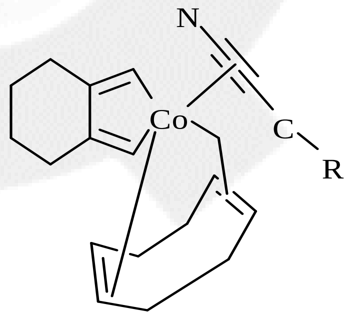
(a) Oxidative addition
(b) Oxidative coupling
(c) Migratory insertion
(d) Reductive elimination

12. Among the given structure some are possible intermediate for the cyclotrimerization reaction given in the scheme-I. Select the right structures and arrange them in correct sequence in which the reaction mechanism in most likely to proceed.

Scheme-I:



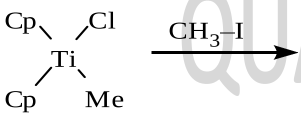
Intermediates:

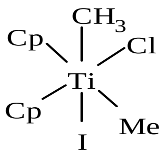
(a)		(b)	
(c)		(d)	
(e)		(f)	

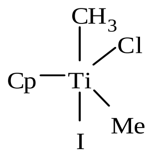
The correct order, sequence are

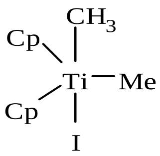
(a) C → A → D → F
(b) E → D → A → C
(c) A → B → C → D → E → F
(d) F → E → C → D

13. The following reaction



(a) 

(b) 

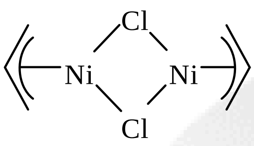
(c) 

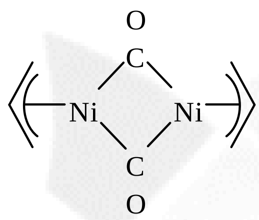
(d) none of these

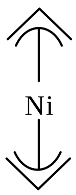
14. Which of the following give fast oxidative addition reaction with CH_3–I.

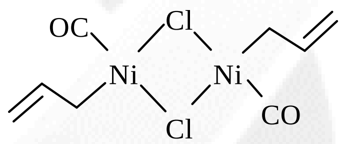
(a) Ir(dppe)(CO)Cl (b) Ir(dmpe)(CO)Cl (c) a and b (d) None of the above

15. Two moles of $Ni(CO)_4$ reacted with two moles of allylchloride with copious evolution of a colourless gas to give a new compound which gave 16 electron count, IR spectra of new compound did not show any bounds in the range of 1650 – 2200 cm^{-1} while chemical analysis after decomposition indicated presence of chlorine M–M bonds are not present in the new molecules.

(a) 

(b) 

(c) 

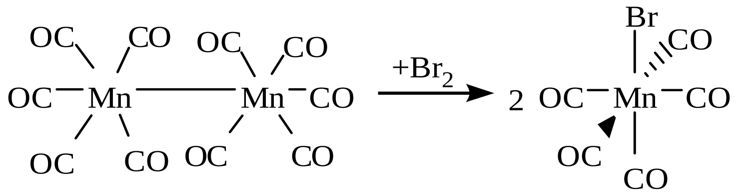
(d) 

×××××

ANSWERS

1. b	2. c	3. a	4. c	5. c	6. b	7. d
8. c	9. b	10. d	11. b	12. a	13. d	14. a
15. a						

Hints & Solutions

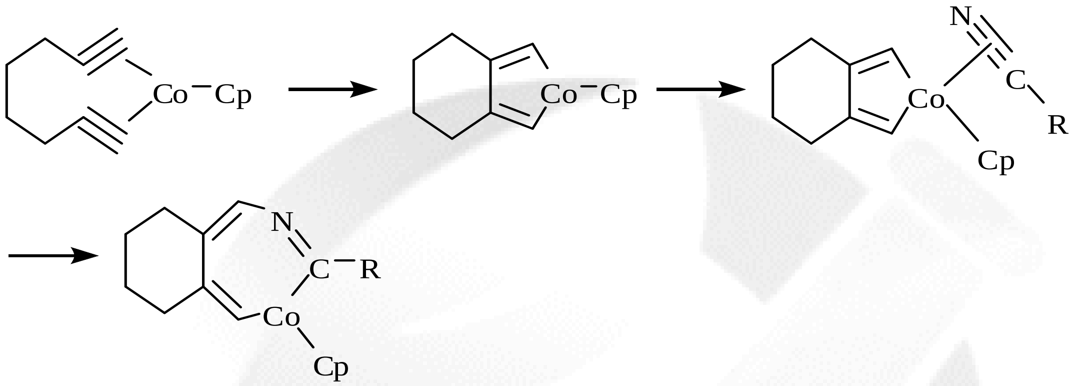
10. 

it is example of oxidative addition reaction.

Correct option is (d)

11. This is example of oxidative Coupling reaction. Because coupling take place in between metal and alkyne group.

Correct option is (b)

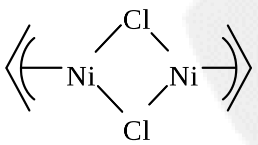
12. 

Correct option is (a)

13. Option (d) is correct because Ti is present in highest oxidation state (+4). and in higher oxidation state system oxidative addition is not possible.

Correct option is (d)

14. Ir(dmpe)(CO)Cl gives fast oxidative addition reaction because dmpe is better donar than dppe.

15. 

per metal = $10 + 3 + 3 = 16\ e^{\ominus}$

Correct option is (a)

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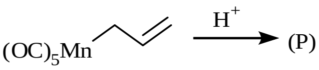
DPP 18 – OMC

1. 

Which of the following statement is true about the product (P)

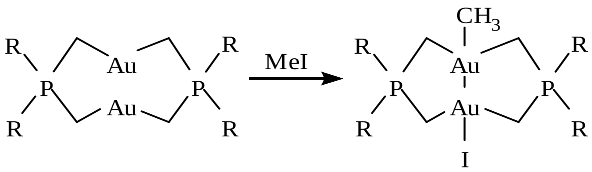
(a) The oxidation state of ‘Mn’ is increased by one unit in the product.

(b) Conversion of h[1]-allyl ligand into h[2]-propene.

(c) Conversion of η^1-allyl ligand into η^3-allyl ligand

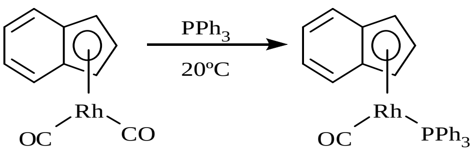
(d) Metal is oxidized.

2. The following reaction is



(a) Oxidative addition	(b) Migratory insertion

(c) b-elimination	(d) Reductive elimination

3. 

The mechanism involved in above synthetic transformation is

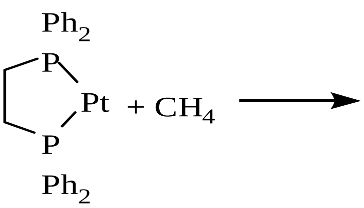
(a) Dissociation of phosphine followed by addition of phosphine

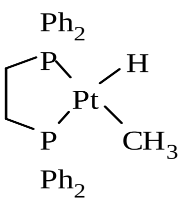
(b) Addition of phosphine followed by dissociation of CO

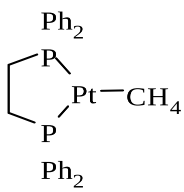
(c) Addition of phosphine, slippage of hapticity from $\eta^5 \rightarrow \eta^3$, followed by dissociation of CO.

(d) Slippage of haptacity $\eta^5 \rightarrow \eta^3$, addition of phosphine dissociation of CO followed by conversion of $\eta^3 \rightarrow \eta^5$

4. Product of the following reaction



(a) 

(b) 

(c) a and b

(d) none of these

5, Oxidative addition of O_2 to $Ir(CO)Cl(PPh_3)_2$, the oxidation state and coordination number of Ir changes respectively by:

(a) 1 and 3	(b) 2 and 2	(c) 3 and 1	(d) 2 and 3

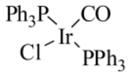
6. Which one of the following will not undergo oxidative addition by methyl iodide?

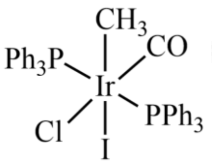
(a) $[Rh(CO)_2I_2]^-$ (b) $[Ir(PPh_3)_2(CO)Cl]$ (c) $[h^2\text{-}CpRh(CO)_2]$ (d) $[h^5\text{-}Cp_2Ti(Me)Cl]$

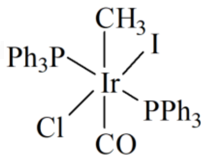
7. Compound that undergoes oxidative addition reaction in presence of H_2 is

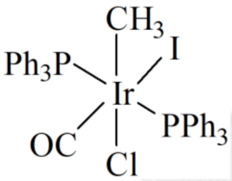
(a) $[Mn(CO)_5]^-$ (b) $[(h^5\text{-}C_5H_5)Mo(CO)_3]^-$

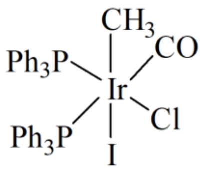
(c) $[IrCl(CO)(PPh_3)_2]$ (d) $[(h^5\text{-}C_5H_5)_2ReH]$

8. Identify the product in the reaction between  and CH_3I going at room temperature via S_N2 mechanism.

(a) 

(b) 

(c) 

(d) 

9. Which of the following statement is not true

(a) For oxidative addition metal should be co-coordinatively unsaturated.

(b) There should be suitable orbitals available for bond formation.

(c) There should not be bonding electron density on the metal.

(d) oxidative addition increases on moving down the group.

10. The reductive reaction is especially efficient for intermediate oxidation states of which d-electron metals.

(a) d^2, d^6 (b) d^8, d^6 (c) d^8, d^2 (d) d^0, d^{10}

11. What change occur in the oxidation state of metal during the reaction.

(a) Increases by 2 (b) Reduces by 2 (c) Increases by 1 (d) Reduces by 1

12. What is the geometry of an intermediate formed when octahedral d^6 complex undergo reductive elimination.

(a) Trigonal bipyramidal (b) Square pyramidal

(c) Distorted trigonal bipyramidal (d) Square planar

13. After reductive elimination the species formed is of which shape and co-oridination number.

(a) T-shaped, 3-co-ordination (b) Square planar, 4-co-ordination

(c) TBP, 5-co-ordination (d) Octahedral, 6-co-ordination

14. After reductive elimination of 6-coordinate d^6 species goes then the reverse reaction of it will be

(a) Oxidative addition (b) Migratory insertion

(c) b-hydride elimination (d) None of these

15 The p-acceptor ligands attached to metal will affects the rate of reductive elimination as

(a) Enhance the rate (b) decreases the rate (c) Remains constant (d) Cannot predicted

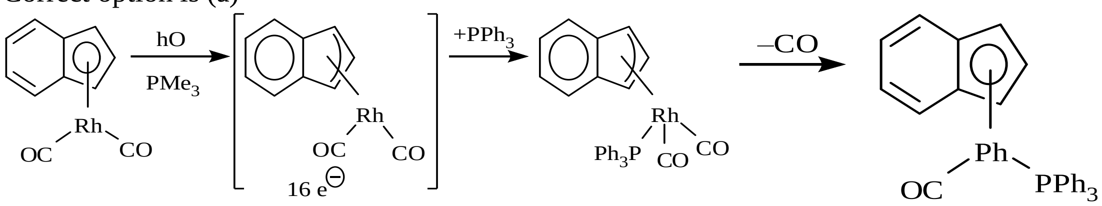
×××××

ANSWERS

1. b	2. a	3. d	4. a	5. b	6. d	7. c
8. a	9. a	10. b	11. b	12. a	13. a	14. a
15. a						

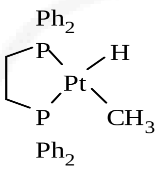
Hints & Solutions

2. it is example of oxidative addition reaction. Because Au is oxidised when CH_3I is added.
Correct option is (a)

3. 

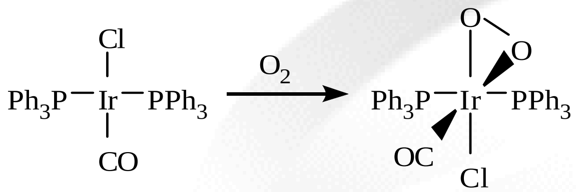
Correct option is (d)

4. It is example of oxidative addition reaction. Because platinum is oxidised after addition of CH_4



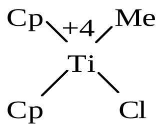
. Correct option is (a)

5. There is change in oxidation state = 2 and coordination number = 2

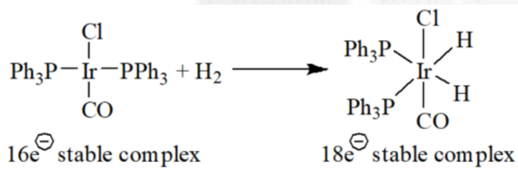


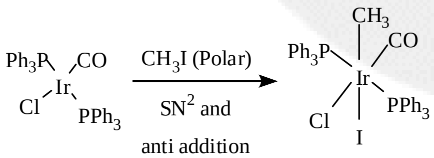
Correct option is (b)

6. Option (d) is not give oxidative addition because it is in higher oxidation state.



7. $[IrCl(CO)(PPh_3)_2]$ is a $16e^{Q}$ complex called as Vaska complex. Only show oxidative addition in presence of H_2. In these H_2 is non polar which take place cis addition.



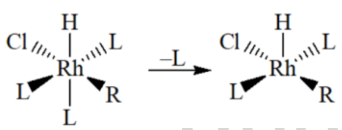
8.  Correct option is (a)

9. Option (a) is not true.

10. Efficient for d^8 metals Ni(II), Pd(II) and Au(III) and d^6 metals Pt (IV), Pd(IV), Ir(III), Rh(III).

11. The formal oxidation state of the metal is reduced by two units in the reaction.

12. Generate a 5-coordinate intermediate, a much more reactive species than the starting 6-co-oridination complex.



13. After reductive elimination, a T-shaped 3-coordinate species is formed.

14. Reductive elimination is the reverse of oxidative elimination vice-versa.
If reductive elimination of 6-co-ord. d^6 species goes then the reverse reaction, oxidative addition of 4 co-ord. d^d species is also expected to go.

15 The π-acceptor ligands attached to metal will enhance the rate of reductive elimination reaction.

QUANTA CHEMISTRY

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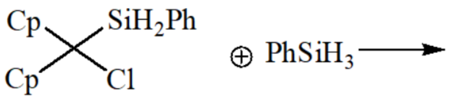
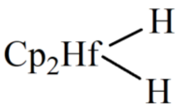
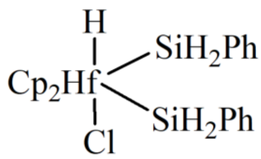
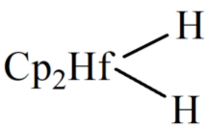
DPP 19 – OMC

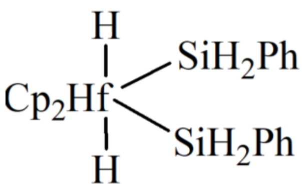
1. The rate of reductive elimination follows the order.
   (a) C – C > H – H > C – H (b) C – H > H – H > C – C
   (c) C – H > C – C > H – H (d) C – C > C – H > H – H
2. In reductive elimination reaction
   (a) Enthalpy increases (b) Entropy decreases
   (c) Entropy increases (d) Enthalpy decreases
3. Which row transition metal undergo reductive elimination faster.
   (a) First row transition metals (b) Second row transition metals
   (c) Third row transition metals (d) All are equal
4. Write the possible intermediate in the following transformation



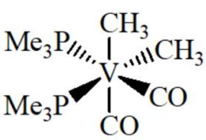
(a) 

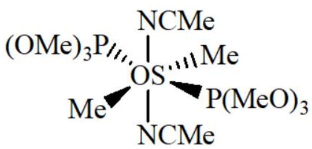
(b) 

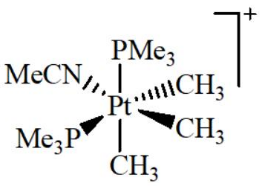
(c) 

(d) 

5. Which one of the following compounds will be most likely to undergo reductive elimination of ethanol.

(i) 

(ii) 

(iii) 

   (a) (i) (b) (ii) (c) (iii) (d) All of these
6. The rarity of reductive eliminations is from which d-electron metal.
   (a) d^6 (b) d^0 (c) d^4 (d) d^8
7. Product of the given reaction will be
   $IrH_2Cl(CO)(PPh_3)_2 \xrightarrow{hv}$
   (a) $IrCl(CO)(PPh_3)_2$ (b) $[IrH_2Cl(CO)]^{2-}$
   (c) $[IrH(cl)(CO)(PPh_3)_2]^{-}$ (d) $[IrCl(CO)(PPh_3)_2]^{2-}$
8. Reductive elimination, the last step in many catalytic cycle such as hydrogenation is to form.
   (a) C – C bond (b) C – H bond (c) C – X bond (d) None of these

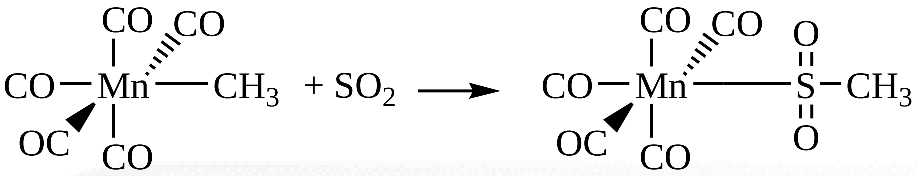
9. What will be the change in oxidation state in migratory insertion reaction?

(a) 2 unit up (b) 2 unit down (c) No change (d) 1 unit up.

10. What will be the ratio of products in CO migration (No ^{13}CO, cis, trans) respectively.

(a) 1 : 2 : 1 (b) 1 : 3 : 0 (c) 1 : 1 : 1 (d) 1 : 0 : 3

11. Name of the given reaction is-

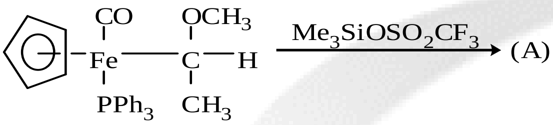


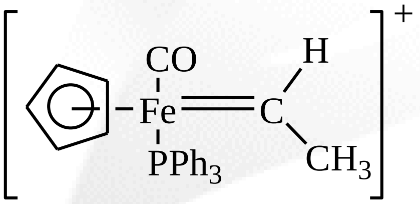
(a) Migration (b) 1, 1 insertion (c) 1, 2 insertion (d) oxidation addition

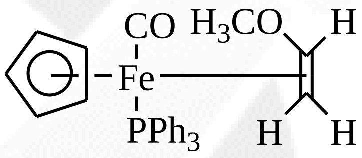
12. What will be the change in the Co-ordination number of the metal in abstraction reaction.

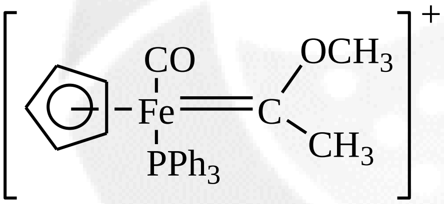
(a) 2 units up (b) 2 units down (c) no change (d) 1 unit up

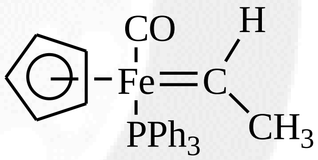
13. What will be the product of the given reaction having α-abstraction.



(a) 

(b) 

(c) 

(d) 

14. What will be the product of the given reaction________

$$(\eta^5-C_5H_5)\,Mo\,(CO)_3[C(=O)CH_3] \xrightarrow{\Delta}$$

(a) $(\eta^5–C_5H_5)Mo\,(CO)_3\,CH_3 + CO$ (b) $(\eta^5–C_5H_5)Mo\,(CO)_4\,CH_3$

(c) $(\eta^5–C_5H_5)Mo\,(CO)_2\,CH_3 + 2CO$ (d) None of these

15. β-hydrogen elimination is the reverse reaction of which reaction?

(a) Oxidation addition (b) Alkene insertion (c) Reductive elimination (d) None of these

×××××

ANSWERS

1. b	2. c	3. a	4. b	5. c	6. b	7. a
8. b	9. c	10. b	11. b	12. c	13. a	14. a
15. b						

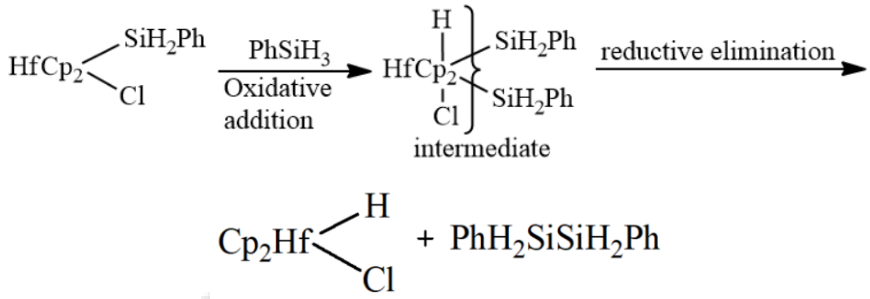
Hints & Solutions

2. The correct option will be (c).

3. First row > Second row > Third row

   This is due to the bond strength, the metal-ligand bonds in first row complexes being weaker than second and third row metals.

4. The cis addition of $PhSiH_3$ forms the intermediate which then undergoes reductive elimination of PhH_2SiSiH_2Ph.



5. (i) is an unstable complex having $15e^-$

   (ii) the eliminating groups are trans to each other.

   (iii) O.S is = x – 3 + 1

   x = + 1 + 3

   x = 4

   O.S is Pt^{+4} and the metal is highly deficient, groups are cis to each other and also obey 18 e^- rule.

6 Reductive eliminations from d^0 early metal centers to form products containing metals possessing d^2 electron configuration are less common.

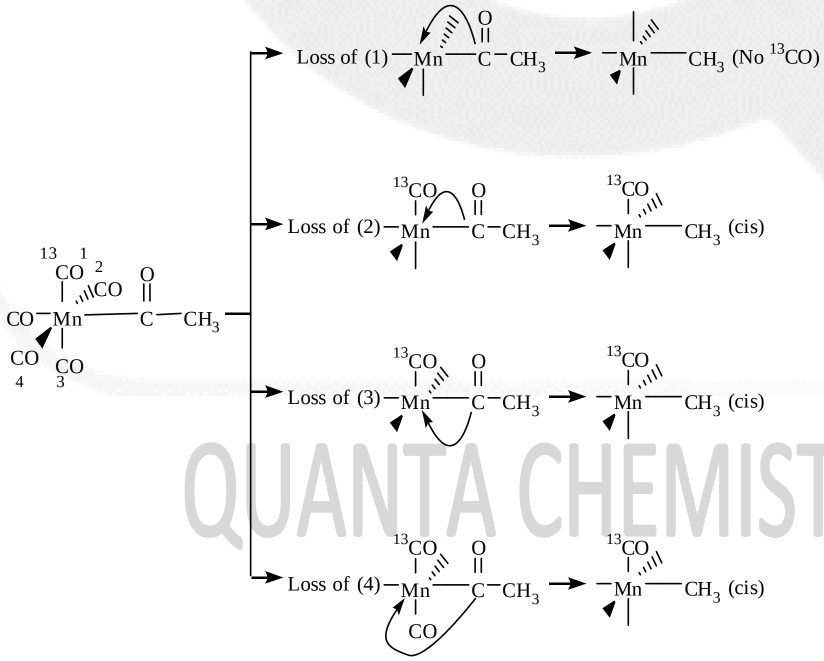
$$IrH_2Cl(CO)(PPh_3)_2 \xrightarrow[h\nu]{-CO} IrH_2Cl(PPh_3)_2 \xrightarrow{-H_2} IrCl(CO)(PPh_3)_2 \xleftarrow{+CO} [IrCl(PPh_3)_2]$$

7.

9. There is no change in oxidation state of metal in migratory insertion reaction.

   Correct option is (c)

10. The CO migration, as a result gives 25% of the product without ^{13}CO label and 75% of the product with labelled ^{13}CO cis to the alkyl group.

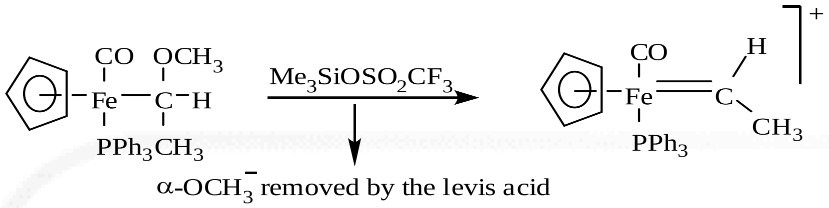


`Correct option is (b)

11. The given reaction is 1, 1 insertion indicating that both bonds to the inserted molecule are made to the same atom in that molecule. In this reaction both Mn and CH_3 are bonded to the sulfur of the inserted SO_2.

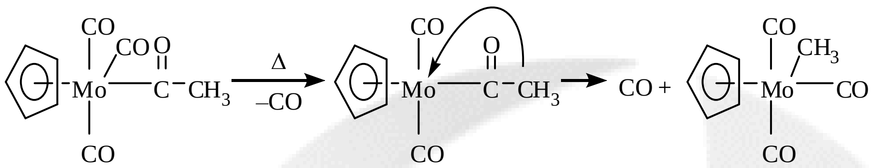
Correct option is (b)

12. Abstraction reactions are elimination reactions in which the Co-ordination number of the metal does not change. In general, they involve removal of a substituent from a ligand, often by the action of an external reagent, such a Lewis acid. Correct option is (c)



13.

Correct option is (a)



14.

Dissociation of CO and methyl migration.

Correct option is (a)

15. β-hydrogen elimination is the reverse reaction of the alkene insertion.

Correct option is (b)